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EFFECT ON THE ENERGY EFFICIENCY OF TUNNEL KILNS MANUFACTURING STRUCTURAL CLAY PRODUCTS OF FLUORIDE EMISSION CONTROL SYSTEMS PHASE III

Final Report

By

POLLUTECH LIMITED

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PHASE III

PROJECT ABSTRACT

The Phase III project involved the firing of test bricks under full scale and normal process conditions in four different plants utilizing tunnel kilns.

Placement of test bricks across diagonal cross-sections of brick hacks facilitated a limited investigation of fluoride loss characteristics versus hack siting.

Comparative effects were observed among the different raw material and additive blends comprising the test bricks.

The effects of density of car packing and other process conditions were observed.

Analytical comparisons were made between dried unfired and fired brick fluoride contents to yield interpretable fluoride changes.

Key conclusions indicated that major factors in controlling fluoride losses were:

1) Material (with calcium content a likely control leader).

2) Car packing density and cross-section (with the lower-loss materials most affected).

Recommended future work would centre on correlation between full scale process fluoride losses and a select group of cationic components (particularly calcium) in the raw materials.

L'EFFET DU RENDEMENT ÉNERGÉTIQUE DES FOURS TUNNELS FABRICANT DES PRODUITS D'ARGILE STRUCTURELS DES SYSTÈMES DE CONTRÔLE DE L'ÉMISSION DE FLUORURE

RÉSUMÉ DU PROJET PHASE III

Le projet Phase III impliquait la cuite de briques expérimentales dans les conditions d'utilisation et celles du processus normal dans quatre usines différentes équipées de fours tunnels.

Le placement des briques d'essai sur des sections transversales diagonales de blocs en briques facilita la recherche limitée des caractéristiques de déperdition de fluorure en fonction du positionnement des blocs.

On observa les effets comparés de différents mélanges de matière première et d'additifs dans les briques d'essai.

Les effets de la densité de la garniture dans les wagons et des autres conditions du processus furent étudiés.

On mena des comparaisons analytiques entre la teneur en fluorure des briques sèches non cuites et celle des briques cuites afin d'obtenir des changements de fluorure se prêtant à l'interprétation.

D'après les grandes conclusions, il semblerait que les facteurs principaux dans le contrôle de la déperdition de fluorure soient:

1) Le matériel (la teneur en calcium étant le grand élément de contrôle).

2) La densité de la garniture dans les wagons et la section transversale (les matériaux à faible déperdition étant les plus touchés).

À l'avenir, on recommande d'étudier la corrélation entre la déperdition de fluorure dans le processus à l'échelle et un groupe choisi de composés cationiques (surtout le calcium) dans les matières premières.

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PHASE III

FINAL REPORT

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1. SUMMARY

1. SUMMARY

The Phase III program was comprised of a number of distinct sub-phases:

- Assembly of material samples from contributing brick companies across Canada
- Cataloguing, weighing and encoding the actual samples
- Planning and coordination of the test firing with the four participating plants
- Transportation, placement and retrieval of test samples
- Assembly of operating data
- Weighing, portioning and grinding of test bricks
- Chemical analysis of bricks
- Data processing
- Interpretation and reporting

The Pollutech project team included Mr. John Nicks, formerly of Domtar. Mr. Nicks coordinated the placement and retrieval of the sample bricks and in addition provided expertise in the interpretation of the data which resulted from this study. All chemical analysis was performed at Pollutech's Oakville laboratory.

Overall results of this study have shown that:

- Fluoride loss in the firing of brick is highly dependent upon the basic raw material.

- Quantity and type of calcium minerals in the basic raw material may relate to reduced Fluoride emissions. Future work would be recommended in the correlation of Fluoride content/emission to Calcium, Magnesium,

Iron, Aluminum, Silicon, Potassium, and Sodium compositions of raw materials.

- Dense settings with maximum cross-section reduce Fluoride losses principally in those materials which do not release Fluoride readily.

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2. PROJECT BACKGROUND

2. PROJECT BACKGROUND

2.1 Introduction To Problem

While the clay brick manufacturing industry is not generally recognized as a major source of industrial pollution, it has been identified as a significant source of gaseous (and occasionally particulate) fluorides. The fluoride emissions are generated by the action of heat, during the kiln firing process, on fluoride and fluorosilicate minerals closely associated with the clay and shale raw materials used in brick manufacturing.

It is well known that the emission of gaseous and particulate fluoride compounds from industrial sources can present some hazard to the environment by:

- endangering the health of agricultural and foraging animals (and in extreme cases, the health of humans)

- causing damage to vegetation (foliage)

- contributing in general to acid rain

Concern has recently been expressed by the various regulatory agencies over fluoride emissions and it is anticipated that if these agencies seek to control such emissions, some Canadian clay brick manufacturers will be required to reduce the evolution of fluoride compounds from their plants.

The kiln firing operation, which is the major production rate determining operation in the total clay brick manufacturing process, is also the major energy cost source in clay brick manufacturing. Most plants operate on a continuous basis using tunnel kilns which burn fossil fuels. Since the rapid escalation in the cost of oil and gas in the early 1970's, the Canadian clay brick industry has actively worked towards the optimization of its kiln firing operation in order to minimize energy consumption within the manufacturing process. It has been noted that between 1972 and 1981, energy consumption per manufactured unit, within the industry, has decreased by nearly 29 percent. The improvement in efficiency has been obtained by carefully balancing burner operation, load movement through the kiln, air movement through the kiln, and recirculation of both hot combustion gases and cold air to give optimum product quality and minimum fuel usage. Due to the delicate balance and control which has been developed, and is now required to ensure the energy efficient operation of dynamic systems such as tunnel kilns, it is anticipated that the incorporation of conventional emission control measures such as scrubbers could result in a serious reduction of the kiln energy efficiencies achieved in recent years. A major loss in energy efficiency would seriously hamper the industry's ability to compete with other construction materials in the marketplace.

It is essential, therefore, that any measures employed to reduce or control atmospheric emissions are selected on the basis of their possible impact on energy efficiency in addition to their efficacy and reliability as anti-pollution devices. In principle, control of fluoride emissions from tunnel kilns, used for manufacturing clay bricks, can be applied at one of the following three stages in the brickmaking process:

- During selection of raw materials - i.e. select raw materials with a potential for reduced fluoride emission and/or incorporate additives to suppress fluoride evolution.

- During kiln firing process - i.e. alteration of the firing procedure to reduce the rate of fluoride evolution.

- At the gas exhaust stack - i.e. by incorporation of conventional scrubber systems (wet or dry).

The results of the Phase I study by the Clay Brick Association which evaluated installations in Germany suggested that flue gas cleaning systems using conventional wet scrubber technology should only be considered as a last resort due to both major capital operating and running costs, and unreliable performance. A preventative approach through raw material alteration and modification and/or the implementation of changes in the firing process to reduce fluoride evolution at its source appear to be the better alternatives, and therefore the purpose of this study.

Fluoride evolution and fluoride emission control procedures as they relate to the clay brick manufacturing process have been studied in great detail in Europe, particularly in West Germany, and it is clear from published literature that alternative techniques which utilize raw material modification and/or alteration of the firing process are potentially available. Not all European scientists however, agree with this approach.

It is recognized that Canadian manufacturing and kiln-firing technology together with Canadian raw materials differ significantly from those used in Europe. The introduction of these European approaches to

North America require significant research on the interrelationship of the thermochemistry of fluoride evolution from Canadian clays and shales with known kiln firing technology and current standard practice. The object of this study was, therefore, to develop guidelines to assist the clay brick industry in selecting energy efficient fluoride control methodology.

2.2 Canadian Clay Brick Manufacturing

The Canadian Clay Brick Industry is made up of twenty-three manufacturing plants across the country from Newfoundland to British Columbia. In recent years these plants have collectively manufactured and/or sold in excess of 600 million brick equivalents per year. Typically, the brick making process requires an energy consumption of approximately 5.5 GJ per thousand brick equivalents (5.2×10^6 BTU per thousand brick equivalents).

The manufacturing process for structural clay products typically comprises the following major activities:

- Excavation of raw material - local clays and shales.
- Crushing and grinding to the desired particle size distribution.
- Addition of modifying ingredients (i.e. additives) - e.g. pigments, barium carbonate for scum control, plasticizers and/or binders.
- Conditioning/tempering with water to produce a suitably plastic mass.
- Forming - by high pressure continuous extrusion through dies of the desired cross-section, followed by cutting to the required size.

- Loading onto kiln cars.
- Drying (in tunnel dryers).
- Firing (in continuous tunnel kilns).
- Unloading, grading, packaging and shipment.

As an impurity in clays and shales, fluorides are widespread. Because fluoride and hydroxyl ions are of nearly equal size and both are monovalent, isomorphous substitution of one for the other can be anticipated in clay mineral structures. In addition, these raw materials also contain many other hydroxyl bearing accessory minerals such as mica, hornblende and apatite, among others, all of which are known to contain strongly-bound fluorine.[1] Coupled with the frequent presence of the mineral fluorspar (CaF_2), these sources provide a potential for fluoride emissions during the ceramic firing cycle.

During the heating stages of the ceramic manufacturing process, the fluoride present in the raw materials is primarily evolved as gaseous hydrogen fluoride (HF) or silicon tetrafluoride (SiF_4), although particulate calcium fluoride (CaF_2) and particulate ammonium fluorosilicate[2] $(NH_4)_2SiF_6$ may also be formed when organic impurities are present.

Early estimates of the contribution of the brick industry to the total industrial fluoride emissions were based entirely on laboratory experiments and assumed that all of the available fluoride in the clay or shale was evolved. It has been clearly demonstrated in recent years [3,4] that only a portion of the available fluoride is in fact emitted during the firing operation.

The relative proportion of fluoride evolved is obviously not the same for every clay fired to the same temperature;[1] it will vary with each raw material and with differences in equipment and operational procedures from plant to plant. Fluoride emission occurs during the firing process

when the fluorine compounds entrained within the body become thermodynamically unstable. While the presence of water vapour trapped within the firing atmosphere appears to be of prime importance, there are several other important controlling factors, namely: (3,4,5,6,7)

- Firing Cycle- The total firing time, the maximum firing temperature and the dwell time between 800°C and the sintering range of the clay.

- Type of Kiln- Tunnel kilns can be expected to be the source of higher emissions than periodic kilns. The high rate of flow of flue gases, air and humidity over the ware at elevated temperatures increases the rate of removal of fluoride. For example, products in the centre of the kiln charge (hack) will lose less fluoride than those on the outer edges of the kiln car due to temperature gradients and less exposure to high velocity gases.

- Kiln Operating Conditions- The kiln atmosphere, air/fuel ratios, type of fuel, air leakage and the degree of gaseous recirculation will influence the rate and extent of fluoride emissions during firing. Passage of hot gases (by recirculation) over the cooled charge may lead to readsorption of a portion of the evolved fluoride.

- The Degree of Compaction of the Product and Particle Size of the Raw Materials- Denser compacts have been shown to evolve less fluoride than less dense or more porous products. Similarly, finely-ground raw materials yield higher fluoride levels than dense coarse-grained materials. The cross-sectional dimensions of the ware will also influence fluoride emissions.

- Microstructure and Porosity of Product being Fired - Fluoride migration encounters little resistance in porous ceramic materials whereas the presence of densified phases can effectively impede diffusion.

- The Initial Fluoride Content of the Raw Material- Although fluoride emission is not in general stoichiometric, it may be presumed, other conditions being equal, that raw materials high in fluoride content will cause higher levels of emission.

- Calcium Carbonate Content - The presence of finely-divided, naturally occurring $CaCO_3$ and other calcium compounds in the raw materials has been cited as a factor in limiting the level of fluoride evolution (8).

2.3 Previous Phase II Program

Prior to the execution of the study reported herein, Pollutech Limited completed a two stage program under Phase II of the Canmet project to determine fluoride emission rates of the various raw materials and the effect additives to the raw materials to control fluoride evaluation. A summary of the Phase A and B objectives and conclusions follows.

The Phase A program was divided into three sub-sections referred to as milestones, each of which were made up of a number of tasks. The milestones were identified as follows:

- Milestone No. 1

  Since there are thirteen companies operating some twenty-three brickmaking plants across the country and since some of these plants utilize more than one raw material type (either singularly or in blends), thirty representative samples of brickmaking raw material from cooperating manufacturers across the country were collected. These were in the form of single constituent clays and shales, or as blends, and were measured for fluoride content. Analysis was carried out using the most up-to-date pyrohydrolysis techniques, and incorporating duplicate samples and pyrohydrolysis of known reference standards.

- Milestone No. 2

  Upon completion of Milestone No. 1, and review of the data, the selection of up to ten typical samples from the initial survey for more detailed examination commenced. Having selected ten representative samples in cooperation with the Scientific Authority all data available to characterize the kiln profiles used to fire products from the ten selected samples were collected from the cooperating manufacturers. Project staff visited each facility to collect samples and data. A field report for the plants containing all raw material data and kiln operating data was prepared. With this data in hand, samples were forwarded to the Institute Fur Ziegelforschung in Essen (West Germany) for determination of the fluoride evolution characteristics. Project staff attended at the German test facility to observe both the evaluations and the test facility.

- Milestone No. 3

Having received the fluoride emission profile data from the Institut Fur Ziegelforschung in Essen (West Germany), and having determined the methods for using the information to prepare idealized kiln firing schedules in Milestone No. 2 above, the data were employed to derive theoretical optimized firing curves for each sample tested. The theoretical firing profiles were derived to investigate whether minimum fluoride emissions, based upon the data provided, could be attained while minimizing any energy penalty or preferably maintaining and improving energy consumption.

Completion of all of these tasks in Phase A provided a clear indication of what levels of fluoride could be expected, how much fluoride would be released, and whether the fluoride could possibly be controlled within reasonable energy limits. Specific inferences from this work are as follows:

- the analysis of fluoride in various raw materials from a broad sample of Canadian plants showed fluoride levels ranging from 202 ppm to 1163 ppm, with an average fluoride content of 706 ppm (0.07 percent)

- the variation in fluoride content of the raw materials was related to the geographical area from which the raw material was excavated,

- the rate of evolution of fluoride from test brick samples was found to be directly related to the firing temperature, with the most significant fluoride loss at 800°C to 1000°C

- the rate of fluoride evolution varied significantly among the samples tested, ranging from 15 mg/kg-hr to 149 mg/kg-hr, depending on raw material utilized and specific brickmaking practices employed

- in most instances the rate of fluoride evolution was too high to be able to limit the release of fluoride by modification of the firing curve, unless significant reductions in kiln retention time and top firing temperature could be achieved

- gross energy calculations suggest that the energy impact of changing the firing sequence is positive (i.e. savings) for those modifications which result in a decrease in fluoride evolution

The second phase of this project was instituted to review the use of additives to raw materials to control fluoride evolution during the kiln firing process through an examination of the existing literature, and thereafter by way of experimental tests.

In order to minimize fluoride emissions the raw materials should be selected from either sources low in fluorine content or from sources which exhibit slow rates of fluoride evolution during firing. However, since the supply of brickmaking clays and shales is somewhat limited in Canada and since companies would prefer to use those captive deposits already available, modification of the raw material to limit fluoride evolution by means of additives was considered worthy of a preliminary study. The use of such materials as calcium hydroxide to capture the fluorine and/or ceramic fluxes to reduce firing temperatures and reduce porosity at lower temperatures has been suggested as viable means of achieving these ends. In addition the incorporation of additives to change the particle packing during extrusion forming (such as deflocculants) is equally viable and has been assessed here.

The Phase B program was divided into three sub-sections in order to examine the efficiency of additives and fluxes in inhibiting evolution from selected clay and shale samples. The tasks carried out to complete this phase were as follows:

- Literature Review

  Although literature reviews on the chemistry of fluoride evolution and control mechanisms using conventional scrubber technology was available, there was little information readily accessible on the topics of ceramic fluxes and their combined effect upon firing temperature microstructure development, and fluoride evolution, or on the topic of additive use for immobilization or capture of fluorine in situ. Therefore a literature survey on these topics using a CANOLE computer searching facility was conducted to evaluate current scientific literature on the feasibility of controlling fluoride emissions by such techniques.

- Development of an Experimental Program to Study Reduction of Fluoride Emission

  Based upon the results of the literature review, and in consultation with the Scientific Authority, a series of potential additives were selected for incorporation with typical brick making raw materials. Twenty variations were examined which were aimed at inhibiting fluorine evolution by either fluorine capture, fluxing of the clays to reduce firing temperature, or porosity reduction in the extruded products.

- Experimental Evaluation of Fluoride Release

  Twenty compositional variations on four preselected typical raw materials (i.e. total of 20 samples plus blanks) were prepared for fluoride evolution analysis. Samples were batched in typical ceramic mixing equipment and extruded into cylinders for firing. All samples were fired according to the actual plant firing schedules provided by the relevant manufacturer. The macrostructure and microstructure of the fired extruded bars were subsequently evaluated to determine porosity levels as manufactured.

Completion of all of these tasks in Phase B provided a clear indication of the feasibility of using additives to control fluoride evolution by modification of the chemical structures. Specific inferences from this work are as follows:

- a number of additives are suggested by the literature that could be used to limit fluoride evolution, by complexing with the fluoride to limit release upon firing, or that can be added to the raw material, such that the physical properties of the product are modified, thereby limiting the release of fluoride

- laboratory testing using the various additives did not have a significant effect on the handling of the raw material or the final product

- other than for one sample, the use of additives to complex or trap the fluoride did not result in a significant reduction in fluoride release during firing

3. TECHNICAL WORK PROGRAM AND RESULTS

3. TECHNICAL WORK PROGRAM & RESULTS

3.1 Preparation

Pollutech arranged for the collection of samples of dry bricks from the cooperating brick companies across Canada. This involved the construction and shipment of special shipping crates to assure the integrity of the samples during shipment to Pollutech. Samples were received at Pollutech's Oakville laboratory during a period spanning from several days to several months prior to the first scheduled firing on July 16, 1986 at K1. Those samples which arrived in a wet condition were air dried prior to further handling.

Identification codes were chiseled into several locations on each sample. Samples were then lightly brushed to help preserve the accuracy of the pre and post firing weights. Green brick weights were measured.

At this point green brick samples were randomly selected from each lot of test samples and were then ground to -200 mesh for fluoride analysis.

The remaining green bricks were organized for the four firings scheduled during July and August 1986. Efforts were made to ensure that samples of each of the test lots were available for placement at each of the four test firing locations.

Preparations for chemical analysis included the analysis of National Bureau of Standard opal glass and phosphate rock standards - both certified as to fluoride content. Additionally, spiked brick samples were analyzed throughout the span of the analytical program. Also, catalyst/quartz boat blanks were run throughout the program. The above additional quality control was not funded under this CANMET project but was considered essential to the successful execution of the project.

3.2 Sample Placement & Retrieval

Placement and recovery of sample brick (dried) from Canadian brick plants was executed in four tunnel kilns located in the Toronto-Hamilton area. The kilns used in the firing trials were:

1) **K1.** The kiln was designed by Swindell Dressler, fueled by Natural Gas, under deck fired and oxidizing conditions.

2) **K2.** The kiln was designed by Harrop Ceramic Services, fueled by Natural Gas, under deck fired and alternate oxidizing/reducing conditions (flashing).

3) **K3.** The kiln was designed by Harrop Ceramic Services, fueled with Natural Gas, under deck fired and oxidizing conditions.

4) **K4.** The kiln was designed by Harrop Ceramic Services, fueled by Natural Gas, direct fired with the load on a solid refractory deck and oxidizing conditions.

The push rate at each plant was normal for the load and type of brick being fired during the trials. No unusual conditions were encountered during the trials (i.e. no power failures or interruptions in throughput). All kilns fired the same size of brick - C.S.R.

Placing Samples

Sample locations were suggested as follows:

Two specimens from each sample to be located as follows:

- the top front corner of the kiln car
- the average fired brick location, i.e. located where the brick would show average physical properties
- the bottom of the rear of the kiln car, one up and one into the centre of the hack

There were to be 4 to 6 brick specimens from each sample on a kiln car and the tests would be limited to 2-3 cars in each kiln trial. Following discussions at plant locations we adopted the following placing format. All brick specimens were to be placed as the kiln car was machine set at the brick machine. Two kiln cars were to be utilized; we would avoid placing samples at the extreme ends of the cars and two fire-check keys and/or Buller's rings were placed at each sampling level. For example: after the setting machine set down the first two courses on a kiln car, brick were removed from the second course and replaced with sample brick (height was adjusted to maintain a level setting) and so on until the car was completed. Fire check keys used in the trials were standardized at the K4 Lab and were marked.

In order to determine a suitable location for average fired brick locations we had discussions with operating personnel at the four plants and searched private information available from the K2 lab and the DBR/CBAC Industrial Research Fellowship program.

Eight drawings showing kiln car settings and sample locations are provided in Appendix 2.

Timetable

a) K1

16 samples (96 brick) were placed on kiln car Nos. 15 and 184 a.m. July 16, 1986 with fire check keys as per work sketches. Samples were recovered at the discharging station a.m. July 23rd. Also recovered production brick samples for reference and weight. Production in kiln was C.S.R. size.

b) K2

16 samples (96 brick) were placed in kiln car Nos. 301 and 137 a.m. July 21, 1986 with fire check keys as per work sketches. Samples were recovered and marked by plant personnel and were picked up on July 28th. Also recovered production brick samples for reference and weight. Production in kiln was C.S.R. size.

c) K3

13 samples (72 brick; a number were placed single) were placed in kiln cars 160A and 144A a.m. July 28, 1986 with fire check keys and Buller's rings as per work sketches. Samples were recovered and marked by plant personnel and were picked up on August 5th. Also recovered production brick for reference and weight. Production in kiln was C.S.R. size. Plant personnel checked Buller's rings and tabulated temperatures for our use.

d) K4

16 samples (88 brick) were placed on kiln car Nos. 2006 and 769 a.m. August 5, 1986 with fire check keys as per work sketches.

Samples were recovered and marked by plant personnel and were picked up on August 14th. Also recovered production brick samples for reference and weight. Production in kiln was C.S.R. size.

Firing

Summary of Fire Check Key Readings

Location on Car	K1	K2	K3	K4
Top	85-85-85	53-57-58	53-59-55 1856, 68, 65	76-80-78
Middle	70-70-70	26-23-22-23	40-39-32-35 1829, 26, 14, 07	74-79-77-74
Bottom	70-70-73	39-31-25-23	54-59-49-53 1862, 56, 44, 68	68-67-73-82
Average	75 +	35 -	44 + 1845 F	75 +
Range	15	36	27 59 F	13

1. Buller ring readings in F at same location as keys.

It can be concluded that product from three of the plants would show average physical properties. Product from the K2 plant appeared to be more variable, fired at lower than normal temperatures.

3.3 Kiln Information During Firing of Samples

Kiln information for the four kilns utilized in the test firings is presented in Appendix 3. A summary chart of general kiln information is presented below:

August 1986

Chart of Kiln Information

K1	K2		K3	K4
292' 0"	391' 10"	Kiln length	368' 0"	290' 0"
8 brick	10 brick	Width-brick	9 brick	8 brick
30	39	Cars in kiln[1]	37	30
20.57	28	Cars/24 hrs.	26	21
3,456	4,544	pcs./car[2]	3,456	3,248
71,094	127,232	pcs./24 hrs.	89,856	68,208
144.6	291.9	fired wt.[3]/24 hrs.	214.2	153.0
418.6 Mcf	745.3 Mcf	fuel used/24 hrs.	755.3 Mcf	383.2 Mcf
2.95	2.604	Btu's[4] x 10^6/ tonne	3.60	2.55
oxidizing	oxidizing/ reducing cycle	Atmosphere	oxidizing	oxidizing
485	450	P.C. Temp. F[5]	255	477
29,050 cfm @ 916 rpm	33,900 cfm @ 945 rpm	Exhaust Fan[6] rating	25,000 cfm (Est.)	24,000 cfm @750 rpm

Notes:

[1] Car spaces

[2] C.S.R. size

[3] tonnes

[4] 1020 Btu/1000 cu. ft.

[5] Products of combustion

[6] Fan ratings at 70 F and design rpm

When referring to the detailed information contained in Appendix 3, please note the following:

Note:

1) Temperature readings were in most instances interpolated from kiln records during the firing of the brick samples. In addition the temperature readings are crown temperatures except where noted.

2) Exhaust volumes are shown from fan charts and/or as estimated by plant personnel from prior testing and charts.

3) Generally the temperature of the brick load in the kiln will be less than the T.C. temperatures in the heating up phase and more than the T.C. temperature in the cooling phase.

3.4 Post-Firing Preparation

Fired samples were retrieved to Pollutech's Oakville laboratories, inspected for damage, weighed and portioned. Half of each sample was grounded to -200 mesh for fluoride analysis, the remaining half sample was retained for possible future physical testing by CANMET.

All ground samples were retained in sealed plastic containers with sufficient ground sample for multiple chemical analyses and future investigation.

The only damage revealed on firing was to the H samples. This lot experienced black coring and severe bloating in all four kilns.

3.5 Chemical Analysis

3.5.1 Analytical Procedure

The pyrohydrolysis apparatus, as depicted schematically in Figure 1, generates the concentrate for the follow-up fluoride analysis and consists of the following major components:

- quartz tube furnace
- steam generator
- air supply
- condenser tube
- sample collector

To start the procedure the condenser was connected to the tube furnace exhaust for the collection of the steam condensate. A polyethylene bottle containing 5 ml of the alkaline absorbent solution was placed at the end of the condenser, with the end of the tube submerged. The quartz tube furnace was then preheated to 400°C.

The quartz combustion boat and 100 mg brick sample, as previously prepared in accordance with Section 3.1.1, was placed at the mid point of the tube furnace. The temperature at this point had previously been checked by a rod thermocouple. The steam generator was then started and the tube furnace temperature was increased to 850°C. The system was maintained in this state until 200 mls of condensate had been collected. On average this step took 100 minutes. Duplicate pyrohydrolysis reactions were carried out on each sample analysed.

After collection of the first 200 mls of condensate, the air supply was turned on to collect the few final drops of condensate. The steam generator was then disconnected, and the sample boat was removed. At this point the furnace was turned down to 400°C and the steam generator was reconnected with the clean air purge. This cleaning process continued until the temperature had dropped to 400°C, this took a period of approximately 30 minutes. The condensate was then diluted to 250 mL.

The concentration of fluoride in the condensate sample was determined by standard procedures utilizing an ion-selective electrode. The electrode was calibrated against a standard reference solution, prepared by serial dilution to 0.1 mg/L, 1.0 mg/L and 10 mg/L. An equal part of TISAB (Total ionic strength adjustment buffer)/pH buffer was added to each standard. When the electrode was placed in the mid-range solution of 1.0 mg/L the meter was calibrated after 3 minutes of stirring. Following this the electrode was placed in the 10 mg/L standard, and after 3 minutes of stirring the temperature compensation was adjusted to give a full-scale reading. The meter was therefore set to read 0.1 mg/L to 10 mg/L directly.

Each condensate sample was treated with an equal part of the ISA/pH buffer, and thereafter the mg/L fluoride was determined by direct readout from the meter. This value was then used to determine the fluoride content on a weight ppm basis (mg/kg) as follows:

$$\text{mg/L fluoride} \times \frac{250\ \text{mL sample} \times 1{,}000{,}000\ \text{mg/kg}}{1000\ \text{mL} \qquad 100\ \text{mg sample}} = \text{mg/kg Fluoride (ppm)}$$

Several steps were taken by Pollutech's analytical staff to ensure that the fluoride results were accurate. Quality control procedures were utilized throughout the pyrohydrolysis/analysis stage as follows:

- duplicate tests were run on all samples including both the pyrohydrolysis and ion selective electrode analysis

- analysis of standard reference materials - certified as to fluoride content, was performed along with spiked additions to brick samples to assess recoveries. Standards utilized were:

  - NBS standard #91 : Opal Glass
  - NBS standard #1206 : Phosphate Rock

- combustion boats were run through the pyrohydrolysis procedure with catalyst only - to monitor the system "blank".

- known concentrations of NaF were used to verify the ion-selective electrode procedure

In general the pyrohydrolysis plus ion-selective electrode procedure was found to be very stable.

3.5.2 Results of Chemical Analysis

The results of all chemical analysis are summarized in the Tables 1 to 4 included as Section 7 of this report. The codes **K1, K2, K3 and K4** refer to the 4 kiln test firings in July and August 1986. For actual dates and sample positions see the footnote to Table 1.

The sample identification codes used are composed of a letter and a number. The letter is an identification code which identifies the sequence of placement of the bricks on the cars (i.e. bricks were placed in alphabetical sequence: A-G on the first car and H-N/Q on the second car in each kiln firing). The numerical portion of the code is a cross-reference

to the Phase II of the study. For example, Sample code B-111 is of a material similar in composition to that identified as sample 111 in the Phase II reports.

Table 1 summarizes the raw and processed analytical data for 110°C dried green and fired bricks. Duplicate fluoride analyses are reported and averaged. Average fired fluoride data are combined with weight and moisture loss data to convert fired results to a Comparative 110°C dried green brick basis. Absolute and % fluoride losses are then calculated for each material sample.

Table 2 summarizes the % fluoride loss data from Table 1 for those materials which were fired in all four kilns. Average % fluoride losses for all materials combined are presented for each position and kiln.

Table 3 presents the absolute (mg/kg 110°C dried Green Brick Basis) Fluoride losses and is similar to Table 2 in all other respects.

Table 4 presents the average weight data air dried green and fired for each sample or sample pair.

NOTE: The abbreviation **GBB** used throughout the tables and graphs in Sections 7 and 8 refer to a 110°C dried green brick basis in all cases.

4. DISCUSSION

4. DISCUSSION

4.1 Influence of Material Type

Results of the Fluoride analysis on the fired brick show that Fluoride loss is highly dependent on the specific raw material used in the manufacture of the brick. Samples of unfired brick contained relatively high levels of Fluoride from a low of 700 to a high of 1107 mg/kg (equivalent to 700-1107 ppm). The fired brick displayed a wide range of Fluoride loss/gain in the firing cycle from an apparent gain for a number of specimens to losses in excess of 70%. The following groups raw materials based on percentage Fluoride loss.

One sample, F, identified as a high lime shale indicates no overall change. 5 of 12 specimens showed a gain in Fluoride offset by the remaining specimens which indicated a Fluoride loss. This sample was fired in kilns with brick loads emitting Fluorides and it is possible that the firing conditions inhibited changes in Fluoride in the sample.

Group 1 - Up to 20% (by weight) Fluoride lost in the firing cycle - samples A, C, D, K and L. A weight loss greater than 18% during firing indicated higher calcium contents. These high lime shales had Fluoride levels in the unfired brick of 892 to 938 mg/kg with Fluoride loss on firing of 90 to 200 mg/kg.

Group 2 - From 20% to 50% (by weight) Fluoride lost in the firing cycle. This group consisted of samples G & J, (with lower calcium content), M, and H. This group of materials showed a weight loss on firing of from 7 to 10% which indicates a lower carbonate content. Fluoride levels in the unfired brick were 835 to 1107 mg/kg with Fluoride loss in firing of 225-520 mg/kg.

Group 3 - Over 50% (by weight) Fluoride lost in the firing cycle. This group consisted of sample B, E, and N (with low calcium content). This group of materials showed a weight loss on firing of 7.0% for samples N and E and 12-13% for sample B. Fluoride levels in the unfired brick were 700 and 731 mg/kg for samples B and 1016 mg/kg for Sample N. This mixed group showed a Fluoride loss in firing of 375-525 mg/kg.

4.2 Effect of Additives

Three of the high lime shales tested were also fired with the following additives: a local plastic clay, frit/glass formulation and manganese ore. In all cases, the additives had little effect on Fluoride release, albeit the trials were limited.

4.3 Phase II Project Review

A review of the Phase II analytical work carried out in Essen compares favourably with the present project. Considering the limited size of the sampling and the two year sampling interval from the raw material supply, the results are within acceptable limits.

% FLUORIDE LOSS

Sample No.	Phase II(1)	Present (2)
N-100	55%	34-65%
E-103	90%	50-77%
M-105	37%	12-43%
H-107	50%	34-57%
D"-108	37%	-19%-42%
B-111	58%	36-63%

1) From Progress Report Phase A Milestone 2 March 31, 1985
2) Range of Fluoride Loss From Four Tunnel Kilns.

4.4 Example Of Fluoride Loss During Firing In A Tunnel Kiln

The following is an estimate of Fluoride emissions based on material D" with a weighted percentage loss of Fluoride of 5%.

7,700 kg/hr x .932 g/kg x .05 = 359 g/hr. Fluoride Equivalent (0.79 lbs/hr)

(For an unfired weight of 7.7 tonnes/hour into the kiln, 932 mg/kg Fluoride content in the shale and an 5% loss of Fluoride during firing.)

4.5 Influence Of Kiln Placement And Operating Conditions

The samples were fired in tunnel kilns in four different plants during July-August 1986. The kilns were of similar design and construction - built over a period of approximately 15 years by two major U.S. kiln builders. The kilns were fired with natural gas, three kilns were under deck fired and the fourth kiln was direct fired with brick set directly on a solid deck.

At the time of the tests all kilns were loaded with the same size of brick (3 core CSR). Three kilns were fired under oxidizing conditions and the fourth kiln was on cycle firing (i.e. oxidation/reduction or flashing). It was noted that the kiln on flashing showed oxygen readings in the kiln of 8 to 11.5% through the preheat and firing zones indicating that excess fuel was being rapidly oxidized downstream from the flashing zone.

The firing/cooling cycles were quite similar in the four kilns as throughput time was in the range of 34-35 hours. However, the graphs of the firing curves show some major differences as follows:

KILN CROWN TEMPERATURE READINGS VS TIME

Kiln No.	Time Through 1350-1600F	Time Through 1600-1800F	Total Through[1] 1350-1800F
K1	5.0 hrs.	2.5 hrs.	7.5 hrs.
K2	1.5 hrs.	1.5 hrs.	3.0 hrs.
K3	4.5 hrs.	4.0 hrs.	8.5 hrs.
K4	1.5 hrs.	5.0 hrs.	6.5 hrs.

NOTE: Previous work concluded that the majority of Fluoride was released in this temperature range (725-1000C).

A review of kiln curves and Fluoride loss data, by material, in the four different kiln settings, indicates that Fluoride release is not highly dependent on present state-of-the-art kiln operating practices. However, the following should be noted:

a) generally, the denser settings displayed a wider range of Fluoride loss ranging from a higher loss in exposed locations around the perimeter of the settings and lower losses in the interior of the setting (e.g. see range of Fluoride loss in Kiln 2 on virtually all the materials between Top, Bottom, and Middle samples). K2 had one of the denser loadings with low void area (12.5%) of the load cross-section and the largest physical cross-section. It is probable that the wide range of Fluoride loss displayed in the denser settings is a function of the large differential in air flow across the brick setting. The reduced air flow through the central mass of the setting retards the removal of chemically combined water, decomposition of carbonates, Fluoride evolution, etc. the transfer of heat to the brick from the hot air/kiln gases and the oxidation process. In addition there is a lag in actual brick temperature through the early part of the heating cycle and rapid temperature increases in the higher temperature zones principally where burners are firing directly into the kiln.

b) There were a number of bricks analysed which showed a net **gain** in Fluoride content during the firing cycle. This phenomena was displayed by high calcium shales in all kilns and it has been proposed that Fluoride has combined with the calcium present in these shales. Note this occurred in the middle of the setting in the under deck fired kiln in several instances and a number of top and middle brick in the solid deck kiln.

In summary, the density of the setting appears to affect the loss of Fluoride during the firing cycle. All settings showed a significant differential in Fluoride loss from middle to perimeter (top and bottom locations) of the load. The density of the setting appeared to be of least influence on raw materials with the higher overall Fluoride loss.

It appears that the high resistance to air/gas flow in the middle of settings is of greater influence on Fluoride loss than the rate of temperature increase in the 1350-1800 F range.

5. CONCLUSIONS AND RECOMMENDATIONS

5. CONCLUSIONS AND RECOMMENDATION

Overall results of this study have shown that:

- Fluoride loss in the firing of brick is highly dependent upon the basic raw material.

- Quantity and type of calcium minerals in the basic raw material may relate to reduced Fluoride emissions. Future work would be recommended in the correlation of Fluoride content/emission to Calcium, Magnesium, Iron, Aluminum, Silicon, Potassium, and Sodium compositions of raw materials.

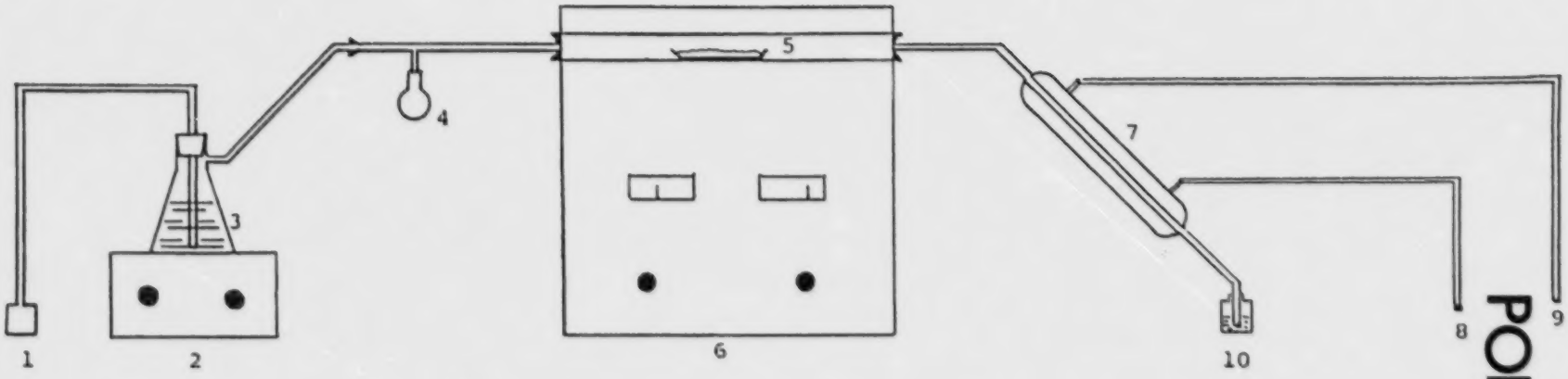
- Dense settings with maximum cross-section reduce Fluoride losses principally in those materials which do not release Fluoride readily.

It should be noted that the majority of the samples were fired in kilns where the fluoride loss characteristics of the load (95 + % of the mass) was significantly different from those of the samples. This did not appear to affect the overall Fluoride loss characteristics of each sample material but it probably affected the magnitude of the Fluoride loss.

6. FIGURES

FIGURE 1: PYROHYDROLYSIS UNIT

1. Air pump
2. Heater/stirrer unit
3. Fluoride free steam generator
4. Condensate trap
5. Sample boat
6. Tube furnace
7. Condensor
8. Cooling water input
9. To drain
10. Caustic sample trap



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7. TABLES

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TABLE 1

RESULTS OF FLUORIDE ANALYSIS - FIRED BRICKS WITH CONVERSION TO GREEN BRICK BASIS (GBB)
(mg F/kg , 110 deg C dry weight basis)

		K1			K2			K3			K4		
CODE	UNFIRED	TF	MI	MB	TF	MI	MB	TF	MI	MB	TF	MI	MB
A - XXX	858	845	1088	823	700	1200	703	1113	1238	850	1083	1012	1033
	925	875	1238	903	850	1125	538	1088	1163	813	1100	1125	800
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	892	860	1163	863	775	1163	621	1100	1200	834	1094	1069	944
% MOISTURE		1.24	1.24	1.24	1.24	1.24	1.24	1.24	1.24	1.24	1.24	1.24	1.24
% WEIGHT LOSS		19.00	19.30	19.50	19.00	19.30	19.50	19.00	19.30	19.50	19.00	19.30	19.50
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COMPARATIVE DATA (GBB)		707	953	705	637	953	507	905	983	692	900	876	772
F LOSS ON FIRING (%)		21	-7	21	29	-7	43	-1	-10	24	-1	2	13
F LOSS ON FIRING (mg/kg GBB)		184	-61	186	254	-61	384	-13	-92	210	-8	16	120
B - 111	731	345	463	358	325	495	333	355	375	388	408	450	360
	731	398	470	348	300	575	388	363	423	398	395	488	408
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	731	372	467	353	313	535	361	359	399	393	402	469	384
% MOISTURE		1.12	1.12	1.12	1.12	1.12	1.12	1.12	1.12	1.12	1.12	1.12	1.12
% WEIGHT LOSS		13.40	11.10	11.20	13.60	13.50	13.60	13.30	11.40	13.80	13.80	13.60	11.10
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COMPARATIVE DATA (GBB)		326	420	317	274	469	316	315	358	343	351	410	345
F LOSS ON FIRING (%)		55	43	57	63	36	57	57	51	53	52	44	53
F LOSS ON FIRING (mg/kg GBB)		405	311	414	458	262	415	416	373	388	380	321	385
C - 109	975	860	1088	795	620	938	800	1395	1313	753	1275	1025	755
	900	1025	1113	810	763	1025	670	975	1200	675	1275	1288	725
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	938	943	1101	803	692	982	735	1185	1256	714	1275	1157	755
% MOISTURE		2.16	2.16	2.16	2.16	2.16	2.16	2.16	2.16	2.16	2.16	2.16	2.16
% WEIGHT LOSS		18.70	19.10	19.00	19.00	18.40	19.80	19.50	19.30	18.60	18.70	18.90	19.00
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COMPARATIVE DATA (GBB)		787	914	667	575	822	605	980	1041	596	1064	983	628
F LOSS ON FIRING (%)		16	2	29	39	12	35	-4	-11	36	-14	-3	33
F LOSS ON FIRING (mg/kg GBB)		151	23	270	362	115	332	-42	-103	341	-127	-25	310
D - 108	925	816	1000	806									
	931	919	994	869									
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	928	868	997	838									
% MOISTURE		2.00	2.00	2.00									
% WEIGHT LOSS		22.2	22.2	22.2									
		---	---	---									
COMPARATIVE DATA (GBB)		692	796	668									
F LOSS ON FIRING (%)		25	14	28									
F LOSS ON FIRING (mg/kg GBB)		236	132	260									

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CODE	UNFIRED	K1 TF	K1 MI	K1 MB	K2 TF	K2 MI	K2 MB	K3 TF	K3 MI	K3 MB	K4 TF	K4 MI	K4 MB
D''- 103	933	781	1050	881	783	1150	600	975	1463	913	1050	1100	800
	925	725	1300	878	735	1100	625	965	1313	875	900	1025	775
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	932	753	1175	880	759	1125	613	970	1388	894	975	1063	788
% MOISTURE		0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
% WEIGHT LOSS		21.80	21.80	21.30	22.00	22.10	21.30	22.20	20.90	21.50	21.70	21.50	21.70
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COMPARATIVE DATA (GBB)		594	928	699	593	885	487	762	1108	708	771	842	623
F LOSS ON FIRING (%)		36	0	25	36	5	48	18	-19	24	17	10	33
F LOSS ON FIRING (mg/kg GBB)		337	4	233	334	47	445	170	-176	223	161	89	309
E - 103	694	205	198	165	178	355	173	213	230	200	320	295	228
	706	243	218	170	173	375	215	240	238	250	285	283	245
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	700	224	208	168	176	365	194	226	234	225	303	289	237
% MOISTURE		1.67	1.67	1.67	1.67	1.67	1.67	1.67	1.67	1.67	1.67	1.67	1.67
% WEIGHT LOSS		6.60	6.70	6.80	6.70	6.70	6.60	6.70	6.50	6.40	6.70	6.70	6.60
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COMPARATIVE DATA (GBB)		213	198	159	167	347	184	215	222	214	287	274	225
F LOSS ON FIRING (%)		70	72	77	76	50	74	69	69	69	59	61	68
F LOSS ON FIRING (mg/kg GBB)		487	502	541	533	353	516	485	478	486	413	426	475
F - XXX	920	813	1350	1050	700	1050	675	1188	1425	748	1238	1200	734
	913	933	1275	1050	709	1188	703	1175	1575	813	1413	1325	835
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	917	873	1313	1050	704	1119	689	1181	1500	780	1326	1263	835
% MOISTURE		1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08
% WEIGHT LOSS		19.80	20.10	19.90	20.00	19.50	19.60	0.00	0.00	0.00	18.40	17.80	18.10
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COMPARATIVE DATA (GBB)		719	1053	852	571	913	561	1194	1516	788	1096	1051	692
F LOSS ON FIRING (%)		23	-16	7	38	0	39	-30	-65	14	-20	-15	24
F LOSS ON FIRING (mg/kg GBB)		207	-146	64	346	4	355	-278	-600	128	-179	-135	224
F''- 104	1000												
	1013	910	925	805	658	1000	670				848	908	945
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	1007	910	925	805	658	1000	670				848	908	945
% MOISTURE		0.83	0.88	0.68	0.86	0.88	0.83				0.88	0.88	0.88
% WEIGHT LOSS		17.8	17.7	15.5	17.0	17.7	16.6				17.3	17.8	17.1
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COMPARATIVE DATA (GBB)		756	769	687	552	832	565				709	754	792
F LOSS ON FIRING (%)		25	24	32	45	17	44				30	25	21
F LOSS ON FIRING (mg/kg GBB)		250	237	319	455	175	442				298	252	215

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CODE	UNFIRED	K1 TF	K1 MI	K1 MB	K2 TF	K2 MI	K2 MB	K3 TF	K3 MI	K3 MB	K4 TF	K4 MI	K4 MB
G - XII	1063	558	713	580	585	973	678	800	963	575	630	760	700
	1063	625	655	655	575	900	675	863	1050	645	725	765	638
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	1063	592	684	618	580	937	677	831	1006	610	678	763	669
% MOISTURE		0.59	0.59	0.59	0.59	0.59	0.59	0.59	0.59	0.59	0.59	0.59	0.59
% WEIGHT LOSS		9.50	9.40	9.50	9.40	9.30	9.30	9.40	9.40	9.30	9.40	9.30	9.30
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COMPARATIVE DATA (GBB)		539	624	562	529	855	618	758	918	557	618	696	611
F LOSS ON FIRING (%)		47	41	47	50	20	42	29	14	48	42	35	43
F LOSS ON FIRING (mg/kg GBB)		524	439	501	534	208	445	305	145	506	445	367	452
H - 107	1063	705	750	570	510	620	488	533	698	650	598	550	590
	1150	735	765	608	523	698	513	625	650	658	670	650	595
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	1107	720	758	589	517	659	501	579	674	654	634	600	593
% MOISTURE		1.03	1.03	1.03	1.03	1.03	1.03	1.03	1.03	1.03	1.03	1.03	1.03
% WEIGHT LOSS		7.60	5.10	7.50	7.20	6.70	7.00	7.50	7.10	7.50	7.20	7.20	7.30
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COMPARATIVE DATA (GBB)		673	727	551	485	622	471	541	633	611	595	563	555
F LOSS ON FIRING (%)		39	34	50	56	44	57	51	43	45	46	47	50
F LOSS ON FIRING (mg/kg GBB)		434	330	556	622	485	636	565	474	495	512	544	551
J - XXI	1100	573	745	550	563	968	645	598	800	530	638	695	583
	1075	618	803	570	473	900	575	700	770	695	750	655	563
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	1088	608	774	560	521	934	610	649	785	613	694	675	583
% MOISTURE		0.78	0.78	0.78	0.78	0.78	0.78	0.78	0.78	0.78	0.78	0.78	0.78
% WEIGHT LOSS		9.20	9.30	9.10	9.40	9.20	9.20	9.40	9.20	9.20	9.40	9.40	9.20
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COMPARATIVE DATA (GBB)		557	703	513	476	855	559	593	719	561	634	617	534
F LOSS ON FIRING (%)		49	35	53	56	21	49	45	34	48	42	43	51
F LOSS ON FIRING (mg/kg GBB)		531	379	574	612	232	529	495	369	527	453	471	554
K - 109	925	850	1088	1013	725	1050	595	873	1150	795	1275	950	850
	938	825	1125	1050	788	1063	513	1000	1125	838	1288	1150	950
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	932	838	1107	1032	757	1057	554	936	1138	816	1282	1050	900
% MOISTURE		1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02
% WEIGHT LOSS		18.50	18.50	18.60	18.70	18.50	19.10	19.70	19.10	18.90	18.90	18.90	19.10
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COMPARATIVE DATA (GBB)		691	913	850	623	872	454	761	932	670	1052	862	737
F LOSS ON FIRING (%)		26	2	9	33	6	51	18	0	28	-13	7	21
F LOSS ON FIRING (mg/kg GBB)		240	18	81	309	60	478	170	0	251	-121	69	194

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CODE	UNFIRED	K1 TF	K1 MI	K1 MB	K2 TF	K2 MI	K2 MB	K3 TF	K3 MI	K3 MB	K4 TF	K4 MI	K4 MB
L - XXI	944	875	1100	913	638	1010	563	903	1150	845	1288	945	800
	931	900	1100	933	643	1000	738	928	1200	850	1188	1175	1300
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	938	888	1100	923	641	1005	651	915	1175	848	1238	1060	1050
% MOISTURE		1.41	1.41	1.41	1.41	1.41	1.41	1.41	1.41	1.41	1.41	1.41	1.41
% WEIGHT LOSS		18.60	18.60	18.40	18.40	18.00	19.00	19.20	19.10	18.60	17.90	18.50	18.70
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COMPARATIVE DATA (GBB)		735	911	786	532	838	536	752	967	702	1034	879	868
F LOSS ON FIRING (%)		22	3	18	43	11	43	20	-3	25	-10	6	7
F LOSS ON FIRING (ag/kg GBB)		203	27	171	406	99	401	185	-30	236	-96	59	69
M - 105	838	688	710	638	513	635	488	580	550	683	600	688	685
	831	868	695	673	650	658	538	658	570	683	698	700	653
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	835	778	703	656	582	647	503	619	560	683	649	694	669
% MOISTURE		1.23	1.23	1.23	1.23	1.23	1.23	1.23	1.23	1.23	1.23	1.23	1.23
% WEIGHT LOSS		6.90	6.70	7.00	6.70	6.80	6.80	6.90	6.60	7.00	6.80	6.90	6.80
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COMPARATIVE DATA (GBB)		734	664	618	550	610	475	584	530	643	613	655	632
F LOSS ON FIRING (%)		12	20	26	34	27	43	30	36	23	27	22	24
F LOSS ON FIRING (ag/kg GBB)		101	170	217	285	224	360	251	305	191	222	190	203
N - 100	1050	563	510	470	325	700	380	475	570	485	423	750	545
	981	500	533	500	450	725	450	505	623	495	483	595	573
	---	---	---	---	---	---	---	---	---	---	---	---	---
	1016	532	522	485	378	713	415	490	596	490	453	673	559
% MOISTURE		0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47
% WEIGHT LOSS		7.10	7.00	7.10	7.20	6.90	7.10	7.10	7.00	7.00	7.20	7.10	7.00
		---	---	---	---	---	---	---	---	---	---	---	---
COMPARATIVE DATA (GBB)		496	487	453	352	667	387	458	557	458	423	628	522
F LOSS ON FIRING (%)		51	52	55	65	34	62	55	45	55	58	38	49
F LOSS ON FIRING (ag/kg GBB)		519	528	563	663	349	623	558	458	557	593	388	493
P - XXI	975										733		
	931	600	743	650	615	1000	598				758	798	750
	---	---	---	---	---	---	---				---	---	---
	978	600	743	650	615	1000	598				746	798	750
% MOISTURE		0.74	0.74	0.74	0.74	0.74	0.74				0.74	0.74	0.74
% WEIGHT LOSS		16.9	17.6	16.5	15.7	16.1	17.0				17.1	16.3	17.2
		---	---	---	---	---	---				---	---	---
COMPARATIVE DATA (GBB)		503	618	548	517	846	501				624	674	627
F LOSS ON FIRING (%)		49	37	44	47	13	49				36	31	36
F LOSS ON FIRING (ag/kg GBB)		475	360	430	461	152	477				354	304	351

POLLUTECH

CODE	UNFIRED	K1 TF	K1 MI	K1 MB	K2 TF	K2 MI	K2 MB	K3 TF	K3 MI	K3 MB	K4 TF	K4 MI	K4 MB
Q - XXX	1038			600									
	1125	900	785	638	705	1000	725				745	820	805
	---	---	---	---	---	---	---				---	---	---
	1082	900	785	619	705	1000	725				745	820	805
% MOISTURE		0.89	0.89	0.89	0.89	0.89	0.89				0.89	0.89	0.89
% WEIGHT LOSS		11.0	11.2	10.9	10.7	11.0	10.8				10.8	10.7	10.8
		---	---	---	---	---	---				---	---	---
COMPARATIVE DATA (GBB)		809	704	557	636	899	653				671	740	725
F LOSS ON FIRING (%)		25	35	48	41	17	40				38	32	33
F LOSS ON FIRING (kg/kg GBB)		272	377	524	446	193	428				410	342	356

NOTE:

K1 July 16,1986

K2 July 21,1986

K3 July 28, 1986

K4 August 5,1986

Firing Postions:

TF = Top Front

MI = Middle Interior

MB = Middle Bottom/Back

POLLUTECH

TABLE 2

RESULTS OF FLUORIDE ANALYSIS - FIRED BRICKS
(% F LOSS , 110 deg C dry weight basis)

	K1			K2			K3			K4		
CODE	TF	MI	MB	TF	MI	MB	TF	MI	MB	TF	MI	MB
A - XXX	21	-7	21	29	-7	43	-1	-10	24	-1	2	13
B - 111	55	43	57	63	36	57	57	51	53	52	44	53
C - 109	16	2	29	39	12	35	-4	-11	36	-14	-3	33
D - 108	36	0	25	36	5	48	18	-17	24	17	10	33
E - 103	70	72	77	76	50	74	69	68	69	59	61	68
F - XXX	23	-16	7	38	0	39	-30	-65	14	-20	-15	24
G - XXX	49	41	47	50	20	42	29	14	48	42	35	43
H - 107	39	34	50	56	44	57	51	43	45	46	49	50
J - XXX	49	35	53	56	21	49	45	34	48	42	43	51
K - 109	24	2	9	33	6	51	18	0	28	-13	7	21
L - XXX	22	3	18	43	11	43	20	-3	15	-10	6	7
M - 105	12	20	26	34	27	43	30	36	23	27	22	24
N - 100	51	52	55	65	34	62	55	45	55	58	38	49
AVERAGE % F LOSS	36	22	36	46	19	43	27	14	33	19	22	35

POLLUTECH

TABLE 3

RESULTS OF FLUORIDE ANALYSIS - FIRED BRICKS
(F LOSS (mg/kg BBB) , 110 deg C dry weight basis)

	K1			K2			K3			K4		
CODE	TF	MI	MB	TF	MI	MB	TF	MI	MB	TF	MI	MB
A - XXX	184	-61	186	254	-61	384	-13	-92	210	-8	16	120
B - 111	405	311	414	458	262	415	416	373	388	380	321	385
C - 109	151	23	270	362	115	332	-42	-103	341	-127	-25	310
D''- 108	337	4	233	334	47	445	170	-176	223	161	89	309
E - 103	487	502	541	533	353	516	465	478	486	413	426	475
F - XXX	207	-146	64	346	4	355	-278	-600	128	-179	-135	224
G - XXX	524	439	501	534	208	445	305	145	506	445	367	452
H - 107	434	380	556	622	485	636	565	474	495	512	544	551
J - XXX	531	379	574	612	232	529	495	369	527	453	471	554
K - 109	240	18	81	309	60	478	170	0	261	-121	69	194
L - XXX	203	27	171	406	99	401	185	-30	236	-96	59	69
M - 105	101	170	217	285	224	360	251	305	191	222	180	203
N - 100	519	528	563	663	349	628	558	458	557	593	388	493
AVERAGE F LOSS (mg/kg BBB)	333	198	336	421	169	441	251	123	350	171	198	321

POLLUTECH

TABLE 4

BRICK WEIGHT CHANGES (A) ON FIRING
ARRANGED BY FIRING LOCATION

CODE	WEIGHTS	K1 TF	K1 MI	K1 MB	K2 TF	K2 MI	K2 MB	K3 TF	K3 MI	K3 MB	K4 TF	K4 MI	K4 MB
A - XXX	Green	2.460	2.460	2.463	2.470	2.468	2.500	2.473	2.455	2.458	2.448	2.460	2.463
	Fired	1.993	1.985	1.983	1.988	1.993	2.018	1.990	1.973	1.988	1.985	1.990	2.008
	Change	0.467	0.475	0.480	0.482	0.475	0.482	0.483	0.482	0.470	0.463	0.470	0.475
	% Change	19.0	19.3	19.5	19.5	19.2	19.3	19.5	19.6	19.1	18.9	19.1	19.1
B - 111	Green	2.198	2.120	2.133	2.200	2.168	2.163	2.173	2.125	2.198	2.168	2.205	2.108
	Fired	1.903	1.885	1.895	1.900	1.875	1.869	1.883	1.883	1.895	1.868	1.905	1.875
	Change	0.295	0.235	0.238	0.300	0.293	0.295	0.290	0.242	0.303	0.300	0.300	0.233
	% Change	13.4	11.1	11.2	13.6	13.5	13.6	13.3	11.4	13.6	13.8	13.6	11.1
C - 109	Green	2.460	2.478	2.495	2.470	2.470	2.478	2.488	2.478	2.473	2.460	2.475	2.463
	Fired	2.000	2.005	2.029	2.000	2.015	2.008	2.003	2.000	2.013	2.000	2.008	1.995
	Change	0.460	0.473	0.475	0.470	0.455	0.470	0.485	0.478	0.460	0.460	0.467	0.468
	% Change	18.7	19.1	19.0	19.0	18.4	19.0	19.5	19.3	18.6	18.7	18.9	19.0
D - 108	Green	2.613											
	Fired	2.034											
	Change	0.579											
	% Change	22.2											
D'- 106	Green	2.365	2.385	2.368	2.395	2.413	2.395	2.385	2.383	2.400	2.383	2.390	2.370
	Fired	1.850	1.865	1.863	1.868	1.880	1.885	1.855	1.885	1.885	1.865	1.875	1.855
	Change	0.515	0.520	0.505	0.527	0.533	0.510	0.530	0.498	0.515	0.518	0.515	0.515
	% Change	21.8	21.8	21.3	22.0	22.1	21.3	22.2	20.9	21.5	21.7	21.5	21.7
E - 103	Green	1.815	1.790	1.775	1.773	1.803	1.785	1.790	1.800	1.783	1.785	1.795	1.775
	Fired	1.695	1.670	1.655	1.655	1.683	1.668	1.670	1.683	1.668	1.665	1.675	1.658
	Change	0.120	0.120	0.120	0.118	0.120	0.117	0.120	0.117	0.115	0.120	0.120	0.117
	% Change	6.6	6.7	6.8	6.7	6.7	6.6	6.7	6.5	6.4	6.7	6.7	6.6
F - XXX	Green	2.495	2.500	2.495	2.493	2.465	2.505				2.456	2.475	2.455
	Fired	2.000	1.998	1.998	1.995	1.985	2.013				2.005	2.035	2.010
	Change	0.495	0.502	0.497	0.498	0.480	0.492				0.451	0.440	0.445
	% Change	19.8	20.1	19.9	20.0	19.5	19.6				18.4	17.8	18.1
F'- 104	Green	2.720	2.730	2.618	2.713	2.725	2.663				2.685	2.675	2.635
	Fired	2.235	2.248	2.213	2.253	2.243	2.220				2.220	2.200	2.185
	Change	0.485	0.482	0.405	0.460	0.482	0.443				0.465	0.475	0.450
	% Change	17.8	17.7	15.5	17.0	17.7	16.6				17.3	17.8	17.1

POLLUTECH

BRICK WEIGHT CHANGES (A) ON FIRING
ARRANGED BY FIRING LOCATION

CODE	WEIGHTS	K1 TF	K1 MI	K1 MB	K2 TF	K2 MI	K2 MB	K3 TF	K3 MI	K3 MB	K4 TF	K4 MI	K4 MB
G - XXX	Green	2.525	2.505	2.520	2.525	2.518	2.508	2.510	2.505	2.520	2.498	2.485	2.480
	Fired	2.285	2.270	2.280	2.288	2.283	2.275	2.275	2.270	2.285	2.253	2.253	2.250
	Change	0.240	0.235	0.240	0.237	0.235	0.233	0.235	0.235	0.235	0.235	0.232	0.230
	% Change	9.5	9.4	9.5	9.4	9.3	9.3	9.4	9.4	9.3	9.4	9.3	9.3
H - 107	Green	1.985	1.938	1.990	1.993	1.988	1.990	1.990	1.983	1.988	1.978	1.983	1.990
	Fired	1.835	1.840	1.840	1.850	1.855	1.850	1.840	1.843	1.838	1.835	1.840	1.845
	Change	0.150	0.098	0.150	0.143	0.133	0.140	0.150	0.140	0.150	0.143	0.143	0.145
	% Change	7.6	5.1	7.5	7.2	6.7	7.0	7.5	7.1	7.5	7.2	7.2	7.3
J - XXX	Green	2.553	2.590	2.480	2.563	2.508	2.563	2.543	2.480	2.493	2.520	2.523	2.490
	Fired	2.318	2.350	2.255	2.323	2.278	2.328	2.305	2.253	2.263	2.283	2.285	2.260
	Change	0.235	0.240	0.225	0.240	0.230	0.235	0.238	0.227	0.230	0.237	0.238	0.230
	% Change	9.2	9.3	9.1	9.4	9.2	9.2	9.4	9.2	9.2	9.4	9.4	9.2
K - 109	Green	2.465	2.465	2.470	2.465	2.465	2.465	2.490	2.479	2.478	2.475	2.475	2.465
	Fired	2.010	2.010	2.010	2.005	2.010	1.993	2.000	2.005	2.010	2.008	2.008	1.995
	Change	0.455	0.455	0.460	0.460	0.455	0.472	0.490	0.473	0.468	0.467	0.467	0.470
	% Change	18.5	18.5	18.6	18.7	18.5	19.1	19.7	19.1	18.9	18.9	18.9	19.1
L - XXX	Green	2.470	2.448	2.470	2.463	2.458	2.468	2.490	2.465	2.430	2.455	2.463	2.465
	Fired	2.010	1.993	2.015	2.010	2.015	1.998	2.013	1.995	1.978	2.015	2.008	2.005
	Change	0.460	0.455	0.455	0.453	0.443	0.470	0.477	0.470	0.452	0.440	0.455	0.460
	% Change	18.6	18.6	18.4	18.4	18.0	19.0	19.2	19.1	18.6	17.9	18.5	18.7
M - 105	Green	1.928	1.933	1.940	1.940	1.925	1.908	1.933	1.925	1.925	1.930	1.925	1.923
	Fired	1.795	1.803	1.805	1.810	1.795	1.778	1.800	1.798	1.790	1.798	1.793	1.793
	Change	0.133	0.130	0.135	0.130	0.130	0.130	0.133	0.127	0.135	0.132	0.132	0.130
	% Change	6.9	6.7	7.0	6.7	6.8	6.8	6.9	6.6	7.0	6.8	6.9	6.8
N - 100	Green	2.605	2.585	2.600	2.600	2.590	2.620	2.593	2.583	2.570	2.603	2.588	2.575
	Fired	2.420	2.403	2.415	2.413	2.410	2.435	2.408	2.403	2.390	2.415	2.405	2.395
	Change	0.185	0.182	0.185	0.187	0.180	0.185	0.185	0.180	0.180	0.188	0.183	0.180
	% Change	7.1	7.0	7.1	7.2	6.9	7.1	7.1	7.0	7.0	7.2	7.1	7.0
P - XXX	Green	2.708	2.720	2.663	2.688	2.663	2.705				2.708	2.680	2.700
	Fired	2.250	2.240	2.240	2.238	2.235	2.245				2.245	2.243	2.235
	Change	0.458	0.480	0.443	0.450	0.428	0.460				0.463	0.437	0.465
	% Change	16.9	17.6	16.5	16.7	16.1	17.0				17.1	16.3	17.2

POLLUTECH

BRICK WEIGHT CHANGES (A) ON FIRING
ARRANGED BY FIRING LOCATION

		K1			K2			K3			K4		
CODE	WEIGHTS	TF	MI	MB	TF	MI	MB	TF	MI	MB	TF	MI	MB
Q - XXX	Green	2.298	2.278	2.299	2.285	2.293	2.285				2.268	2.265	2.258
	Fired	2.045	2.023	2.040	2.040	2.040	2.038				2.023	2.040	2.015
	Change	0.253	0.255	0.250	0.245	0.253	0.247				0.245	0.245	0.243
	% Change	11.0	11.2	10.9	10.7	11.0	10.8				10.8	10.7	10.8

NOTE:

A - Green weights as received, air dried.

Firing Postions:

TF = Top Front

MI = Middle Interior

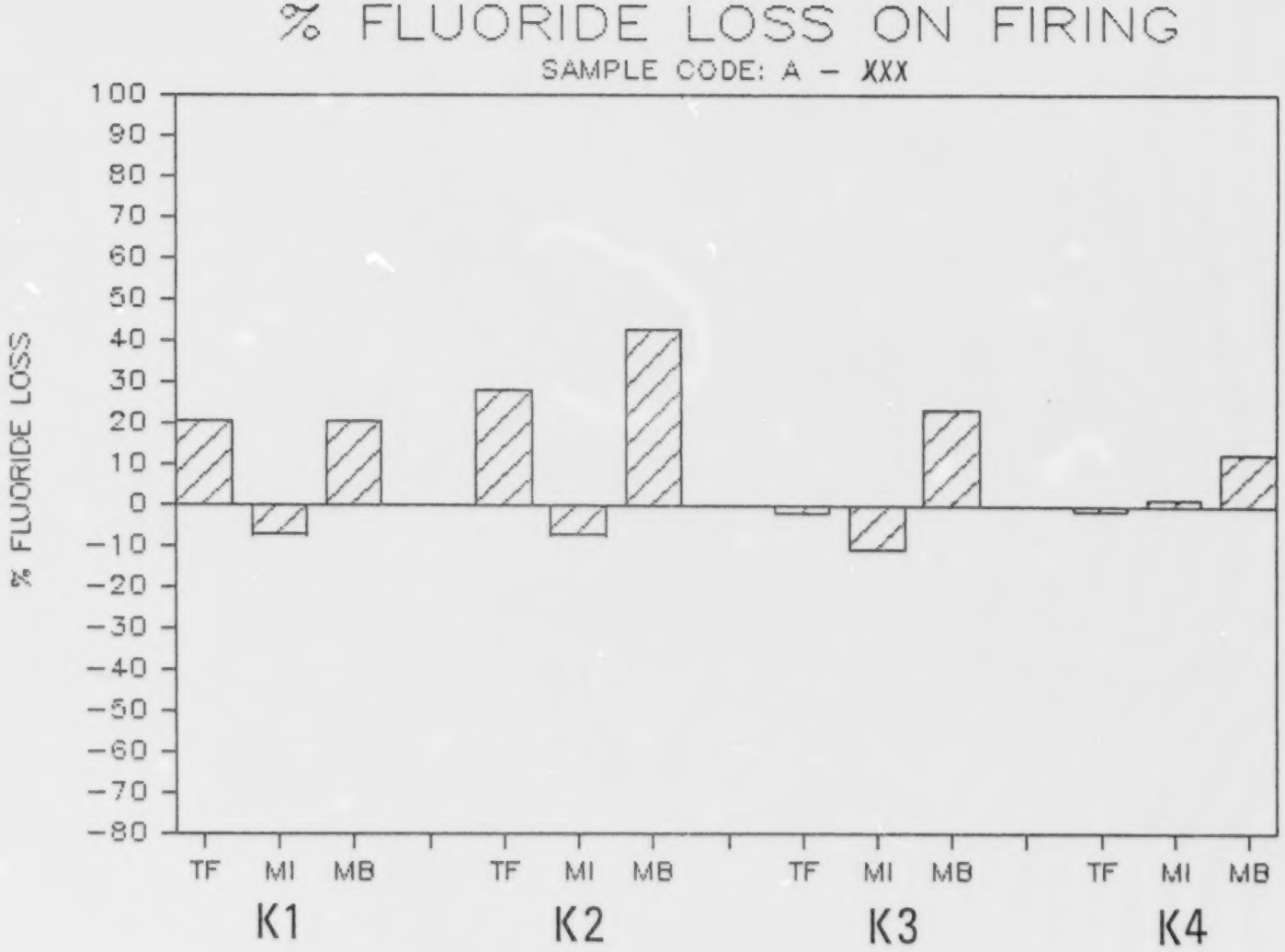
MB = Middle Bottom/Back

8. GRAPHS

- % Fluoride Loss on Firing, by sample
- Fluoride Loss on Firing (mg/kg GBB), by sample
- Material Data
- Average F Loss vs Average % Void in Setting
- Fluoride Loss on Firing vs Position Along Car

POLLUTECH

% Fluoride Loss On Firing by sample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% FLUORIDE LOSS
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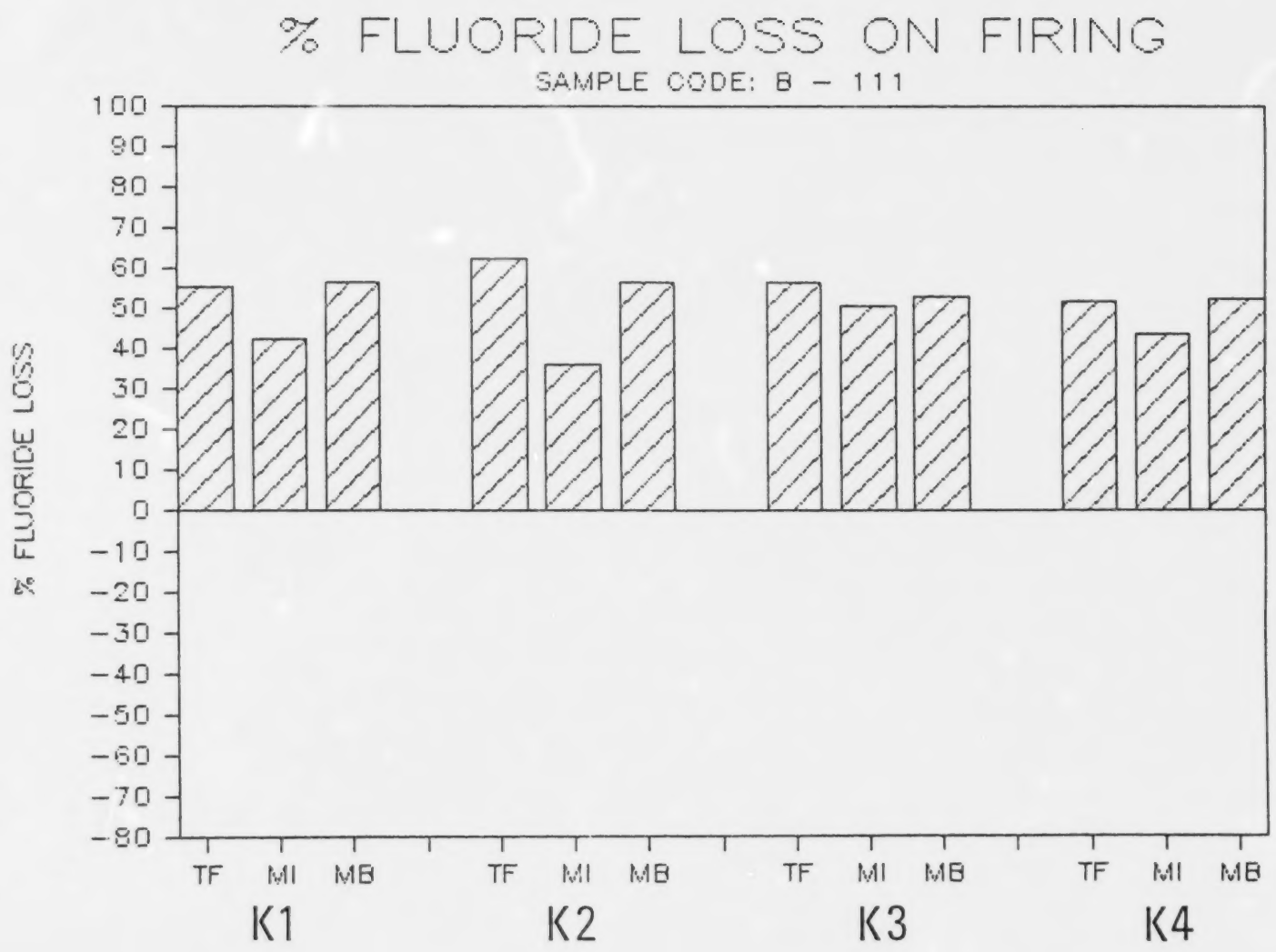
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
TF MI MB TF MI MB TF MI MB TF MI MB
K1 K2 K3 K4

POLLUTECH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SAMPLE CODE: B – 111
% FLUORIDE LOSS
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70
60
50
40
30
20
10
0
-10
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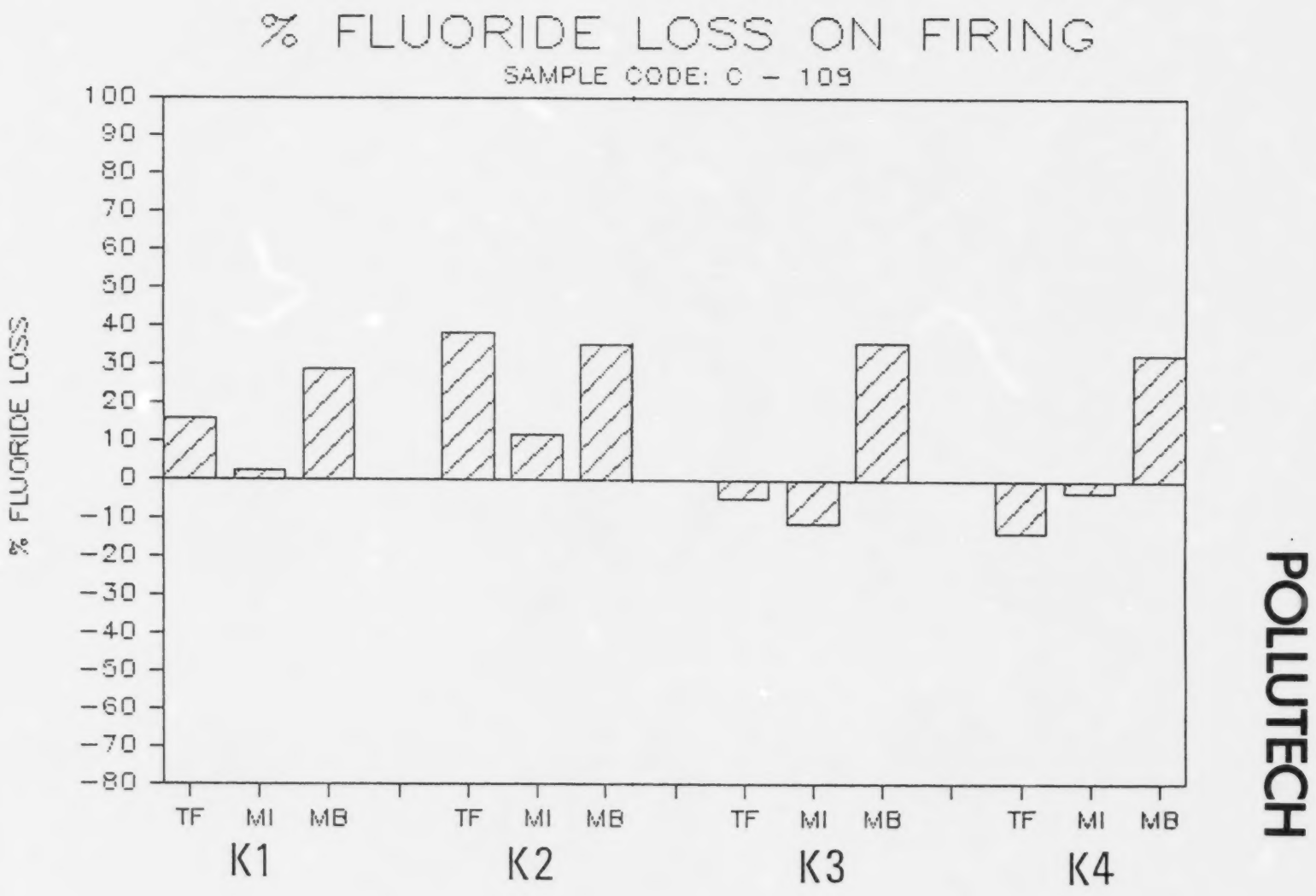
-30
-40
-50
-60
-70
-80
TF MI MB TF MI MB TF MI MB TF MI MB
K1 K2 K3 K4

POLLUTECH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SAMPLE CODE: C - 109
% FLUORIDE LOSS
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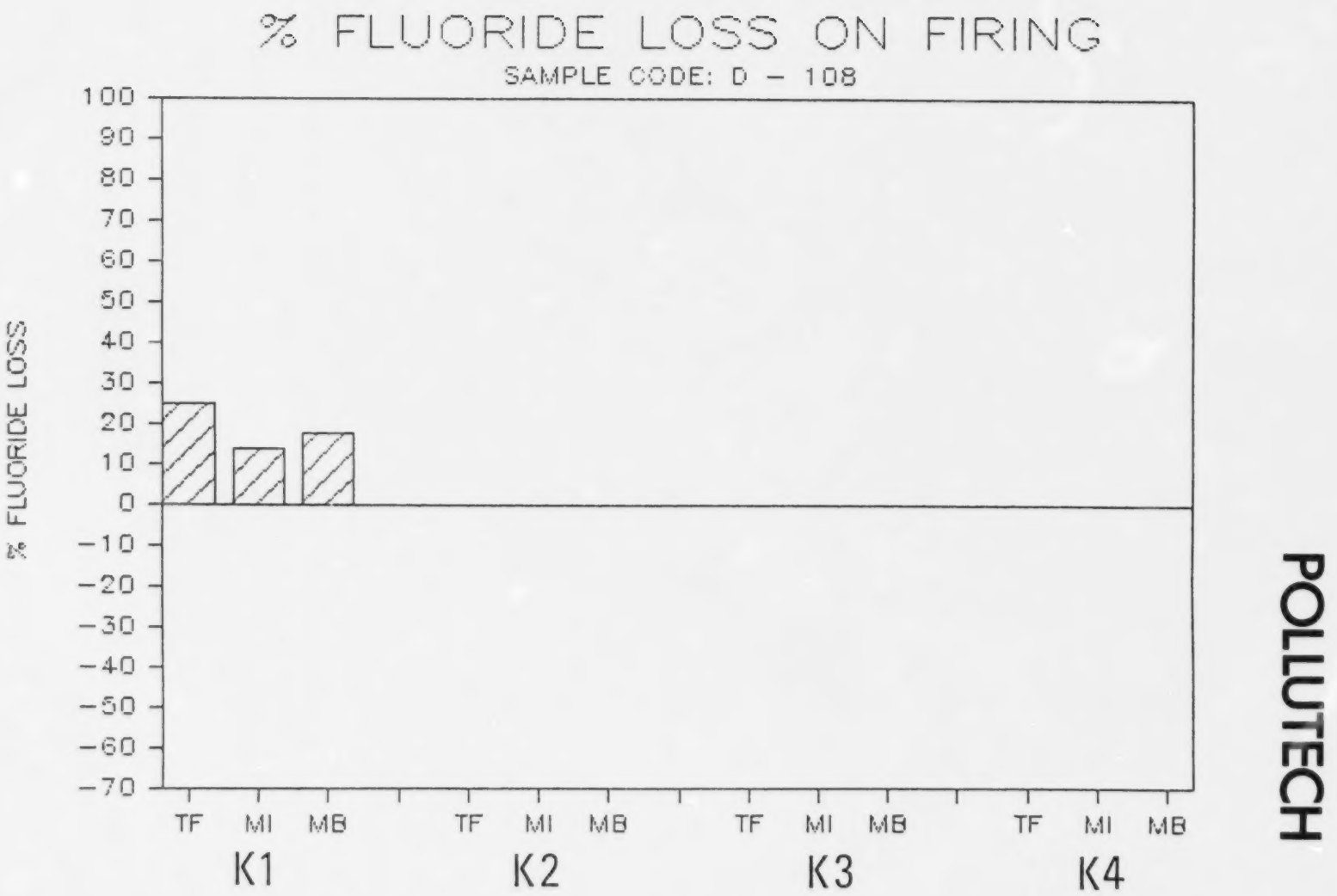
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
TF MI MB TF MI MB TF MI MB TF MI MB
K1 K2 K3 K4

POLLUTECH


% FLUORIDE LOSS ON FIRING
SAMPLE CODE: D – 108
% FLUORIDE LOSS
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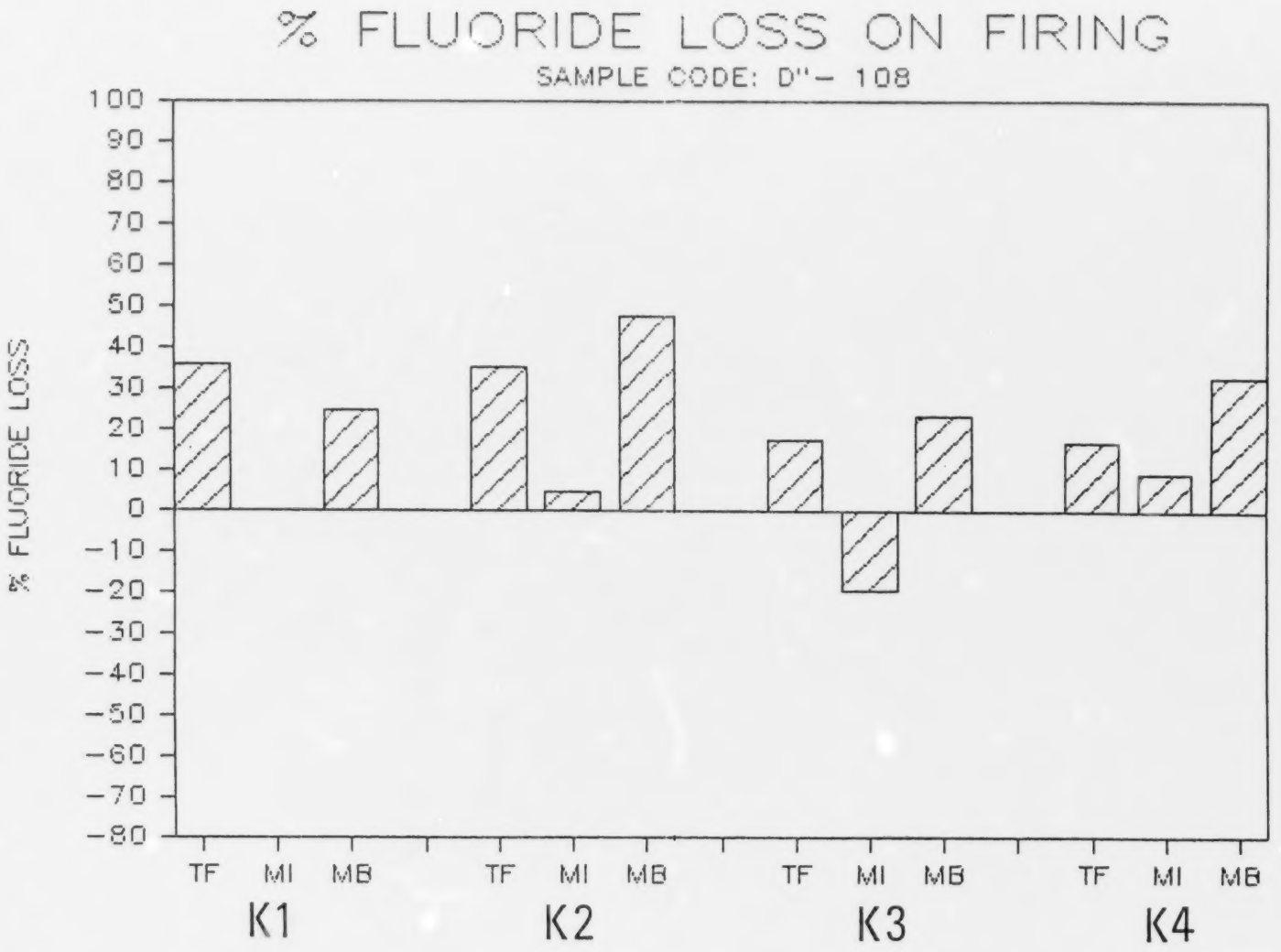
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
TF
MI
MB
K1
K2
K3
K4

POLLUTECH


% FLUORIDE LOSS ON FIRING
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% FLUORIDE LOSS
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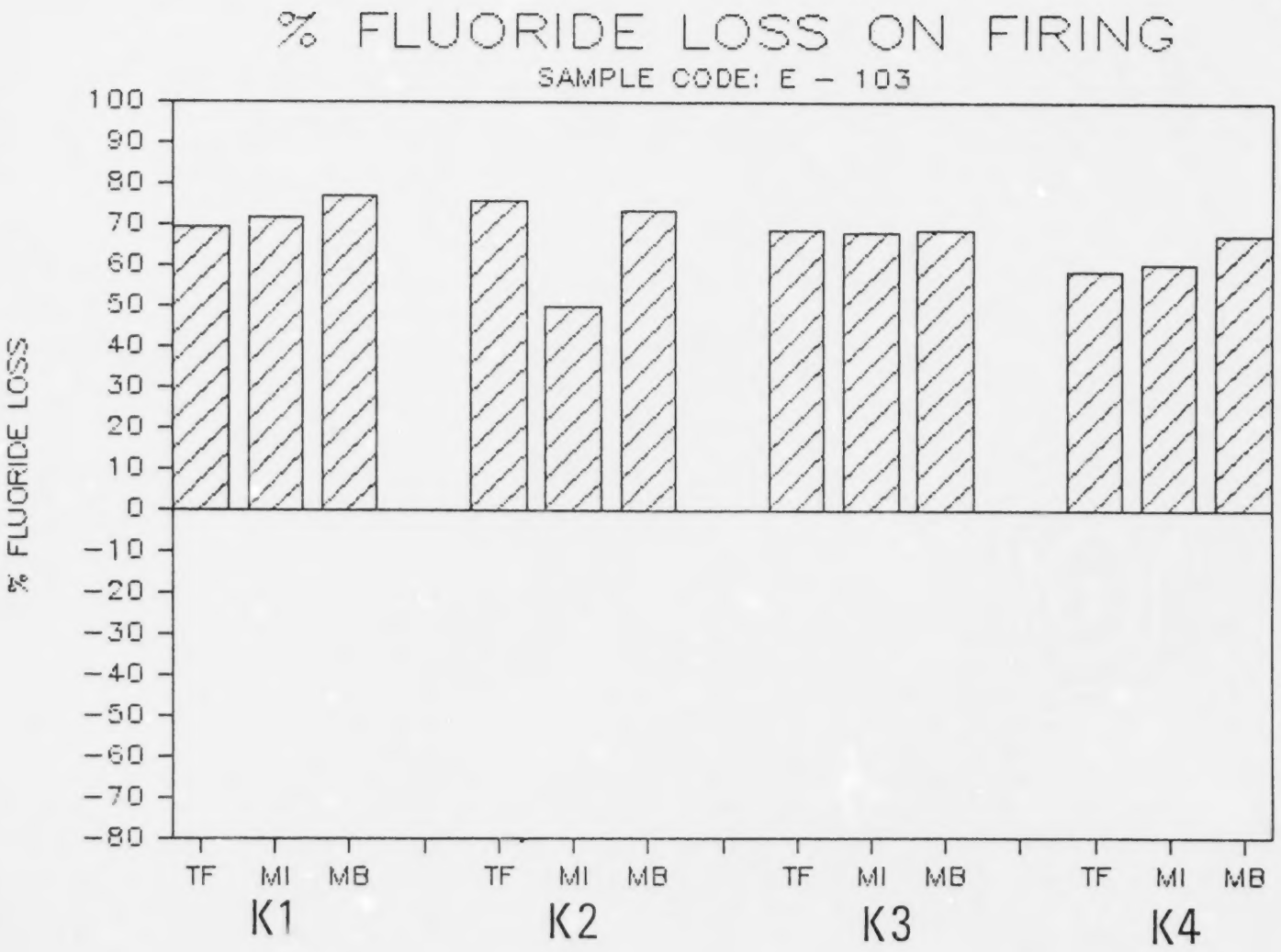
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
TF MI MB TF MI MB TF MI MB TF MI MB
K1 K2 K3 K4

POLLUTECH


% FLUORIDE LOSS ON FIRING
SAMPLE CODE: E – 103
% FLUORIDE LOSS
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90
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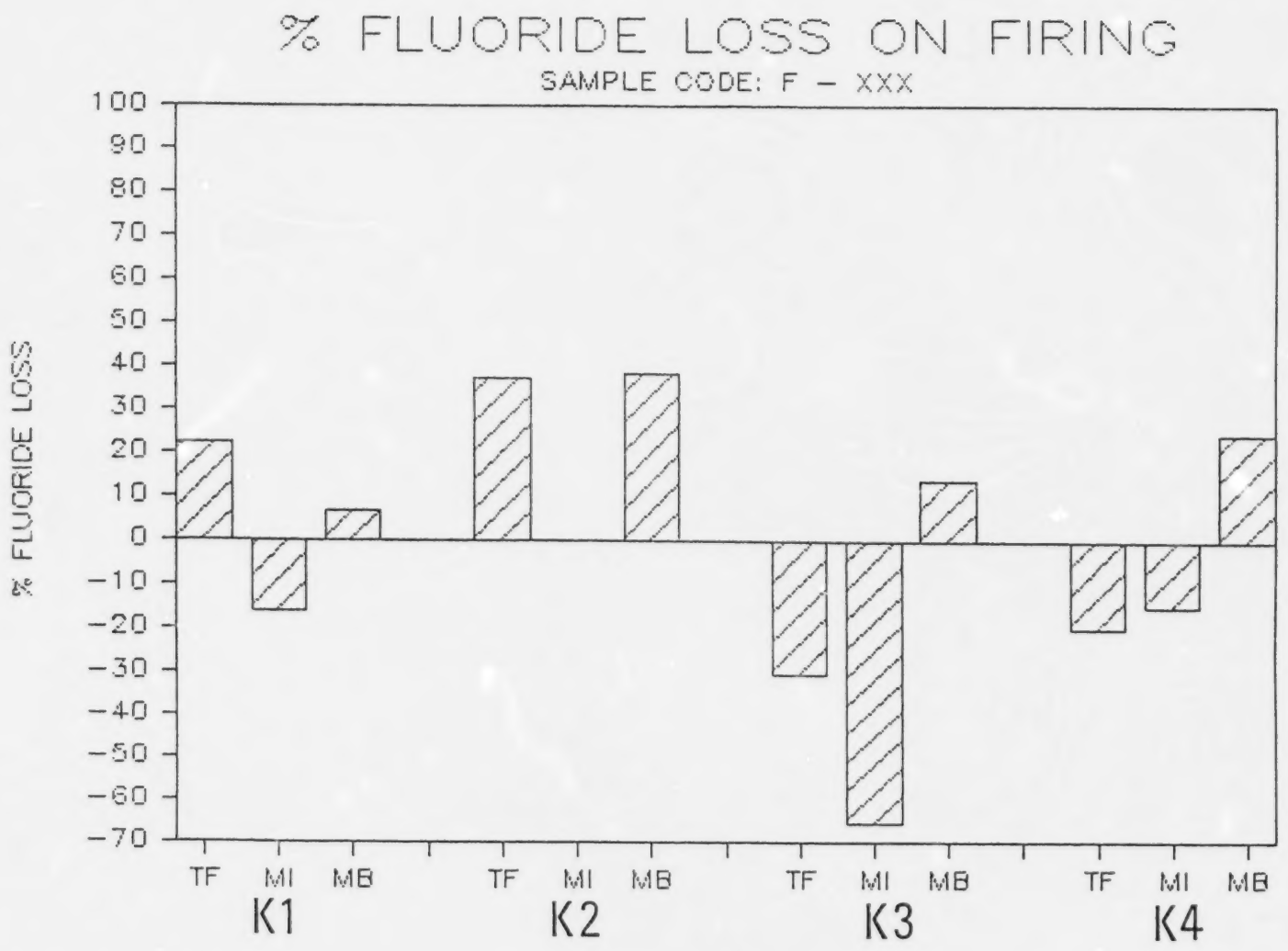
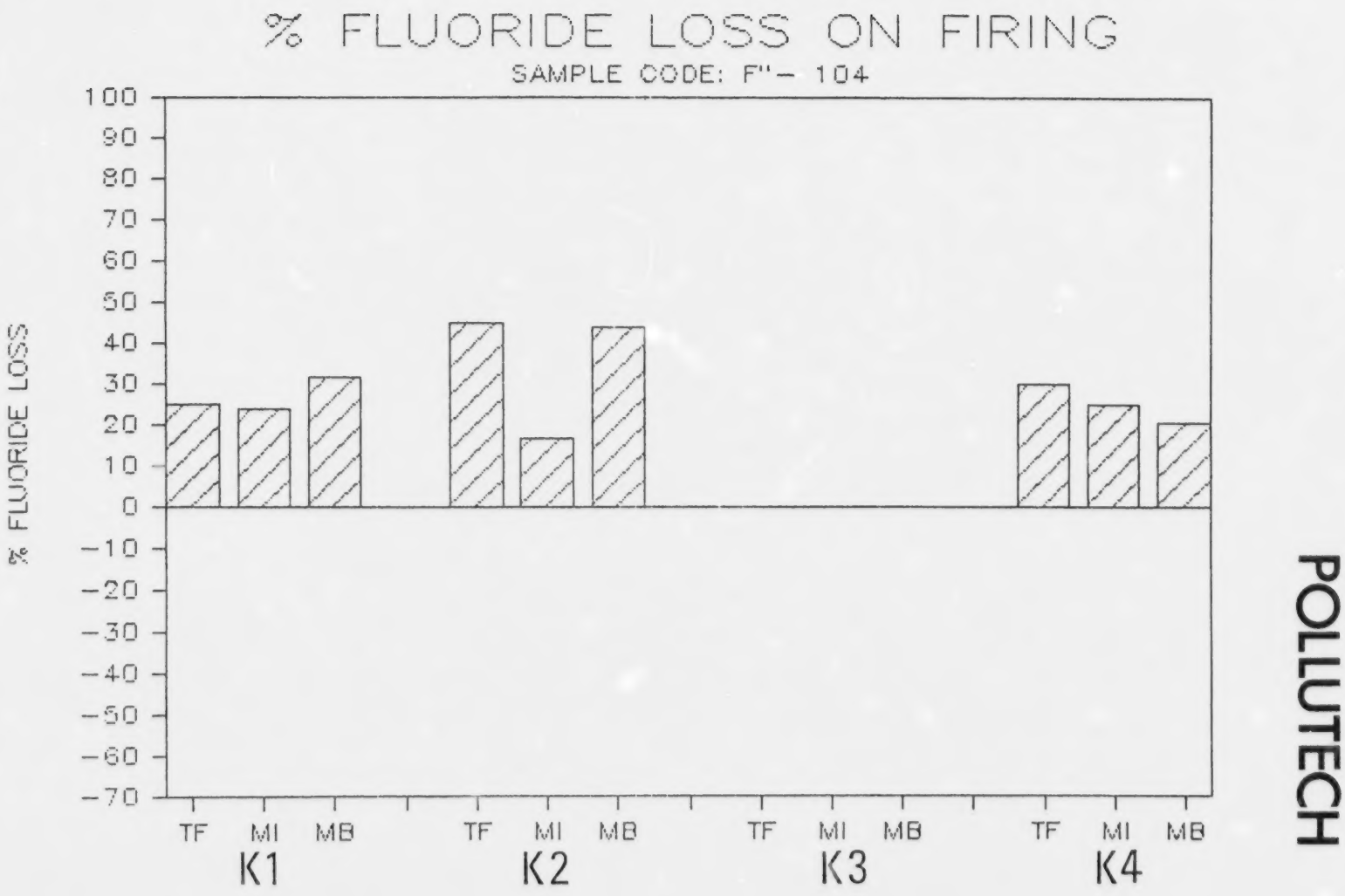
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
TF MI MB TF MI MB TF MI MB TF MI MB
K1 K2 K3 K4

POLLUTECH


% FLUORIDE LOSS ON FIRING
SAMPLE CODE: F – XXX
% FLUORIDE LOSS
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
TF
MI
MB
K1
K2
K3
K4

POLLUTECH


% FLUORIDE LOSS ON FIRING
SAMPLE CODE: F"– 104
% FLUORIDE LOSS
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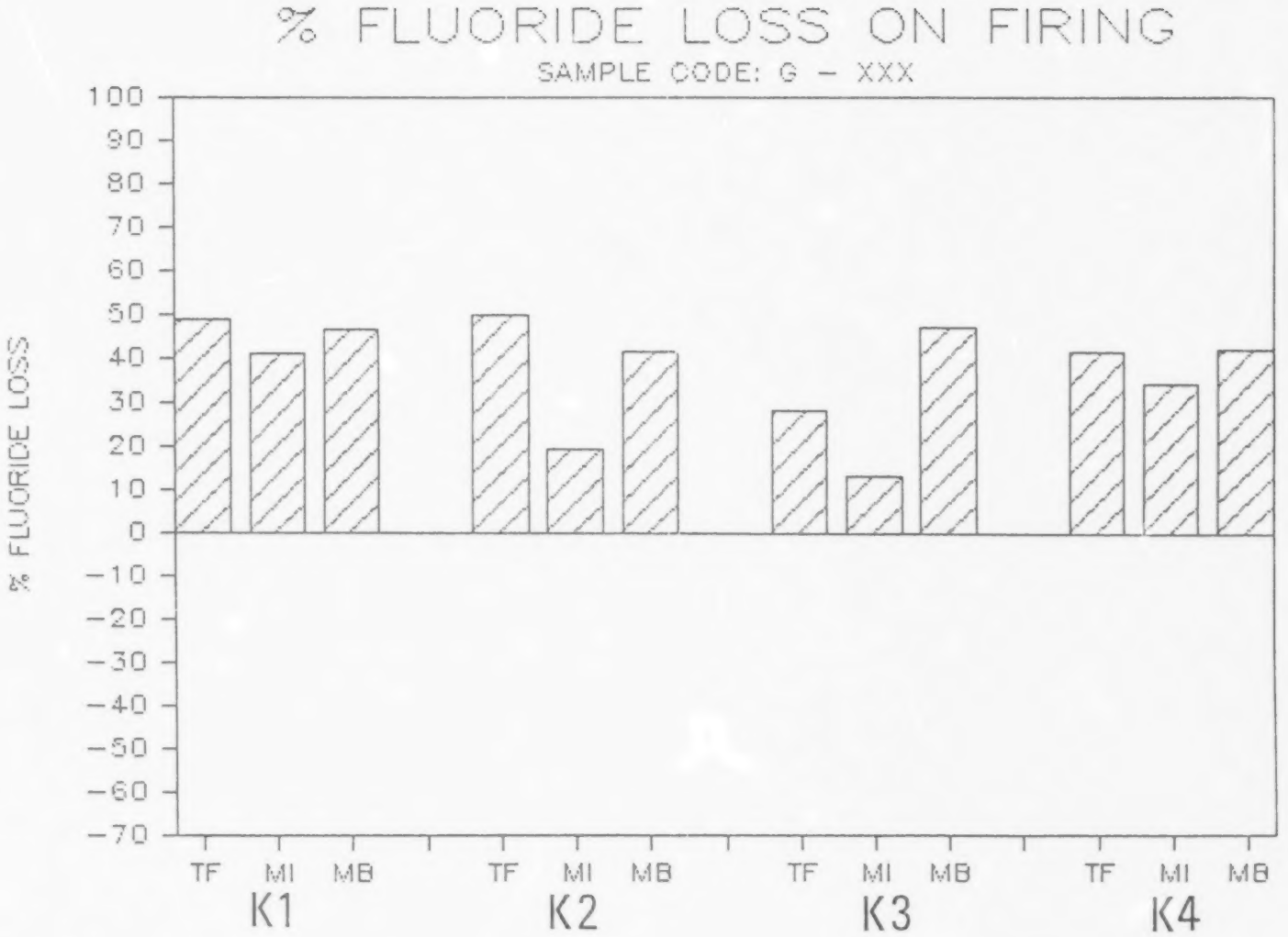
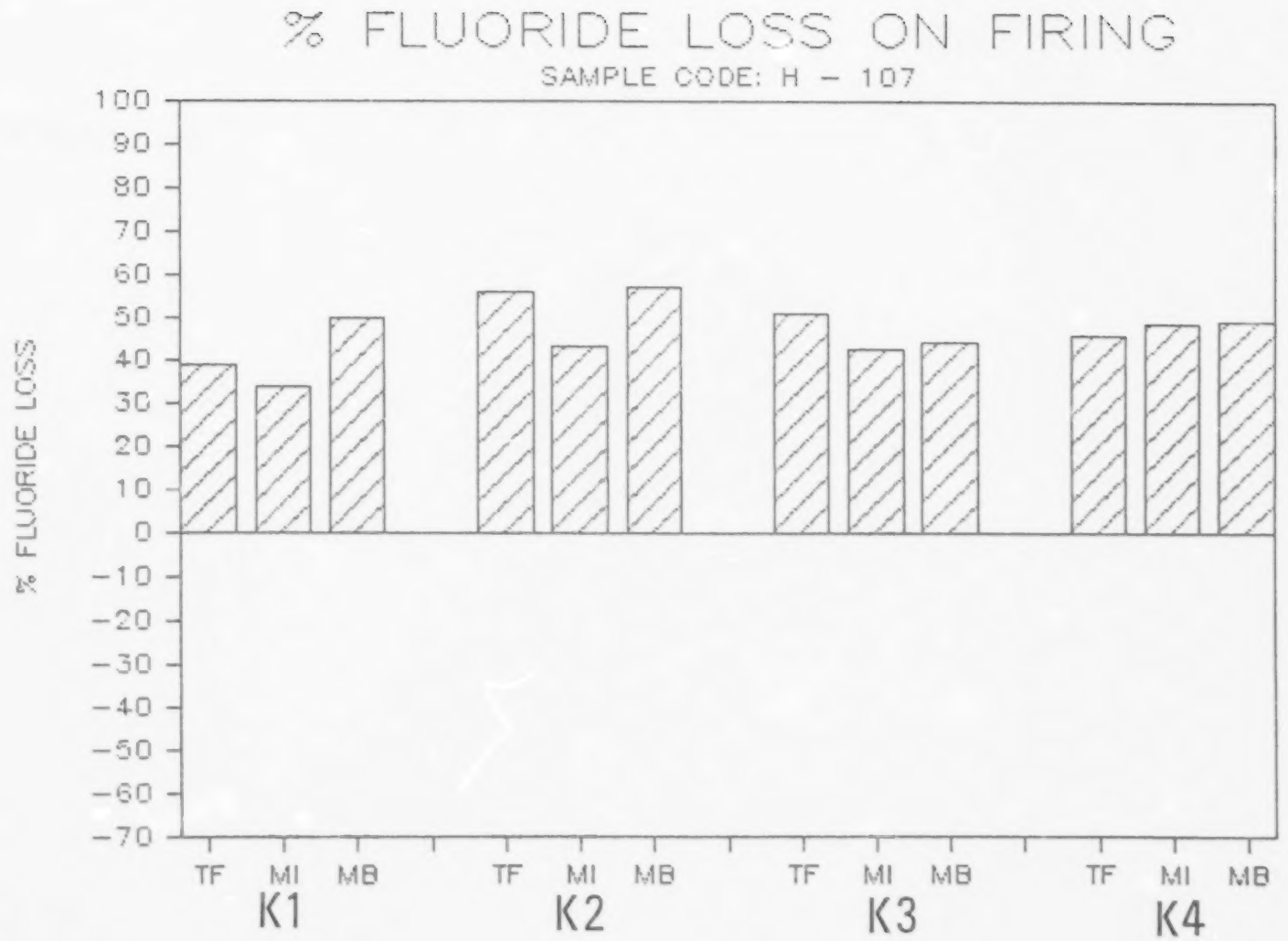
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
TF MI MB TF MI MB TF MI MB TF MI MB
K1 K2 K3 K4

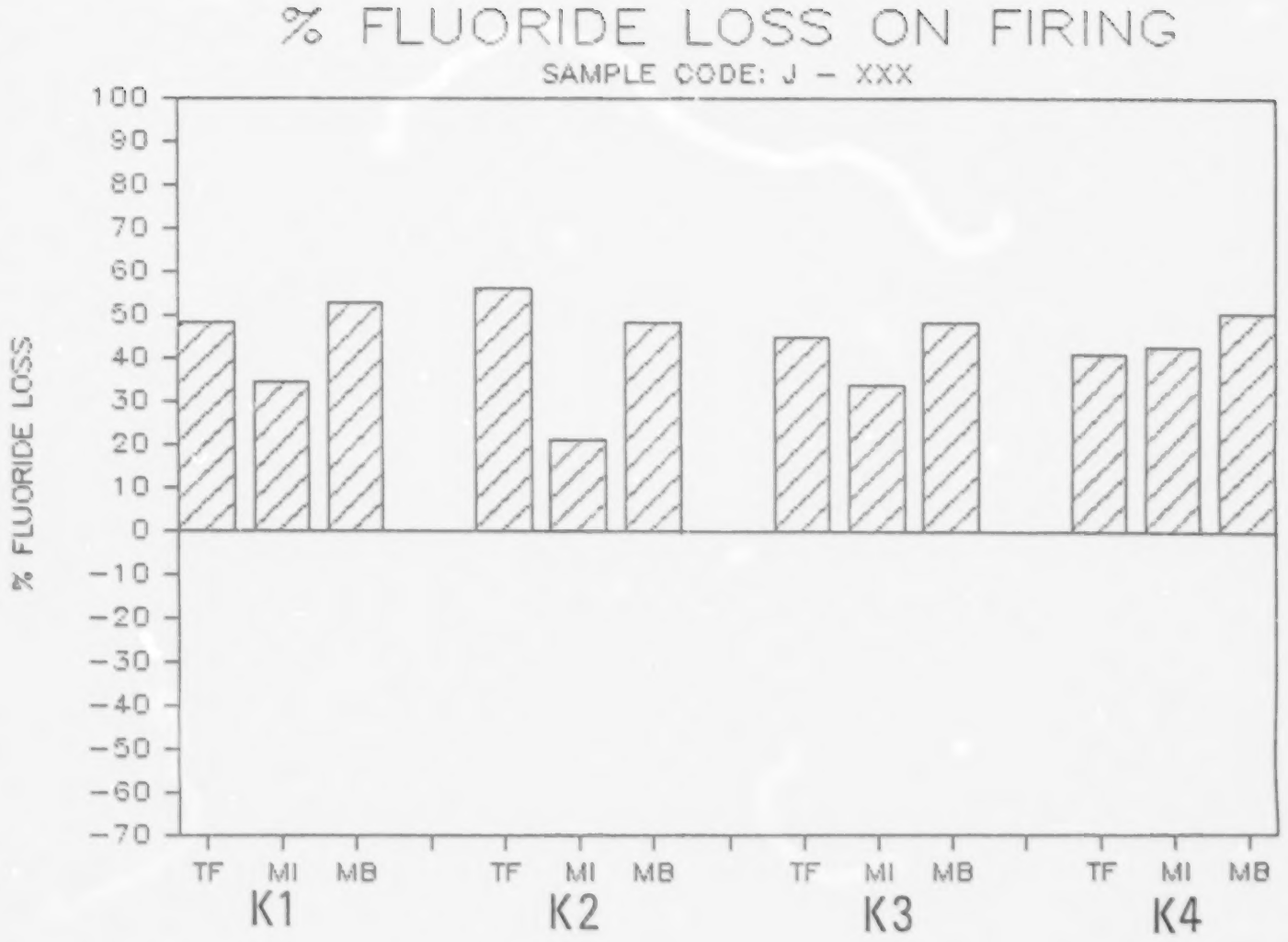
POLLUTECH


% FLUORIDE LOSS ON FIRING
SAMPLE CODE: G – XXX
% FLUORIDE LOSS
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
TF
MI
MB
K1
K2
K3
K4

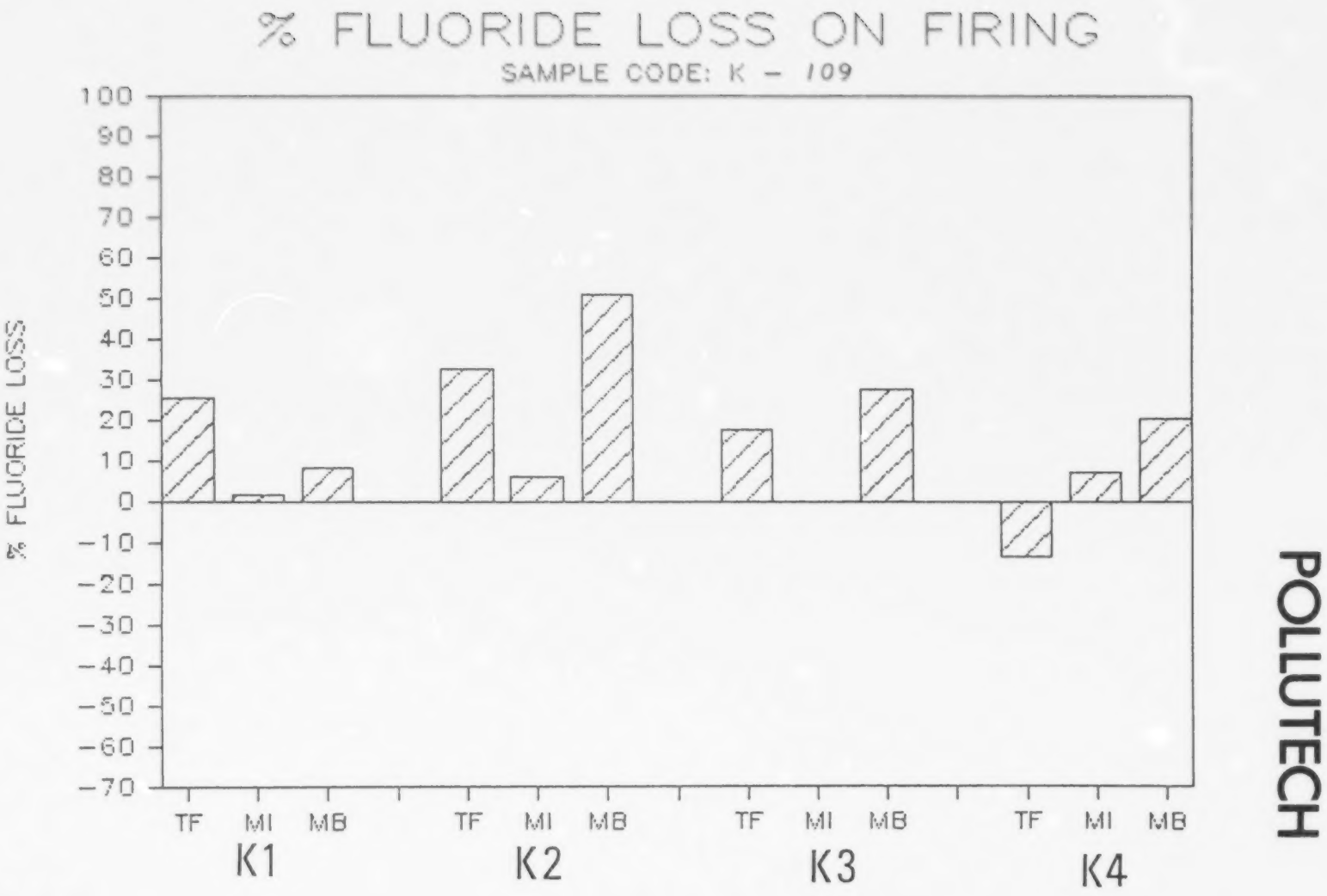
POLLUTECH


% FLUORIDE LOSS ON FIRING
SAMPLE CODE: H – 107
% FLUORIDE LOSS
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
TF MI MB
K1
TF MI MB
K2
TF MI MB
K3
TF MI MB
K4

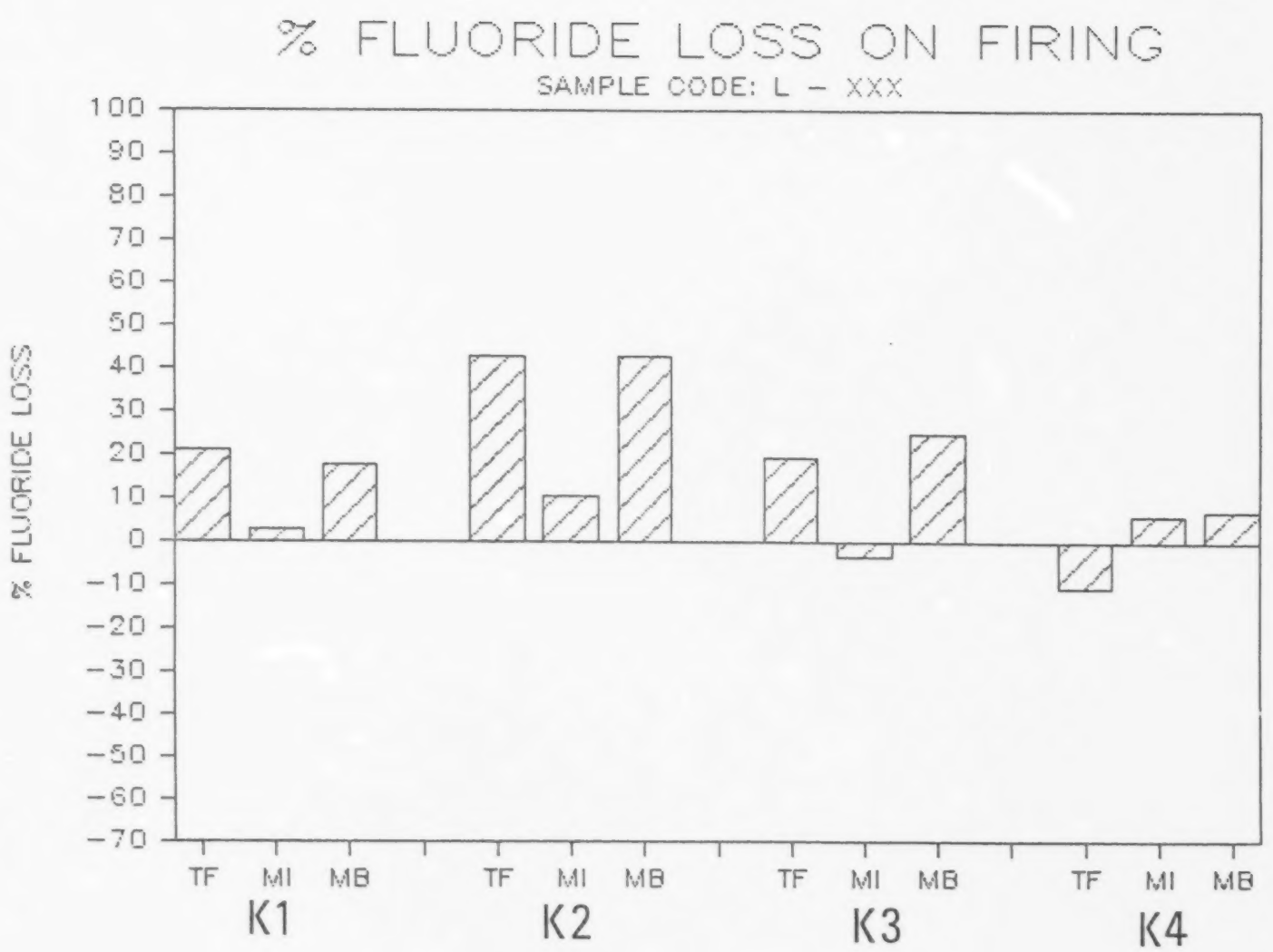
POLLUTECH


% FLUORIDE LOSS ON FIRING
SAMPLE CODE: J – XXX
% FLUORIDE LOSS
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
TF MI MB TF MI MB TF MI MB TF MI MB
K1 K2 K3 K4

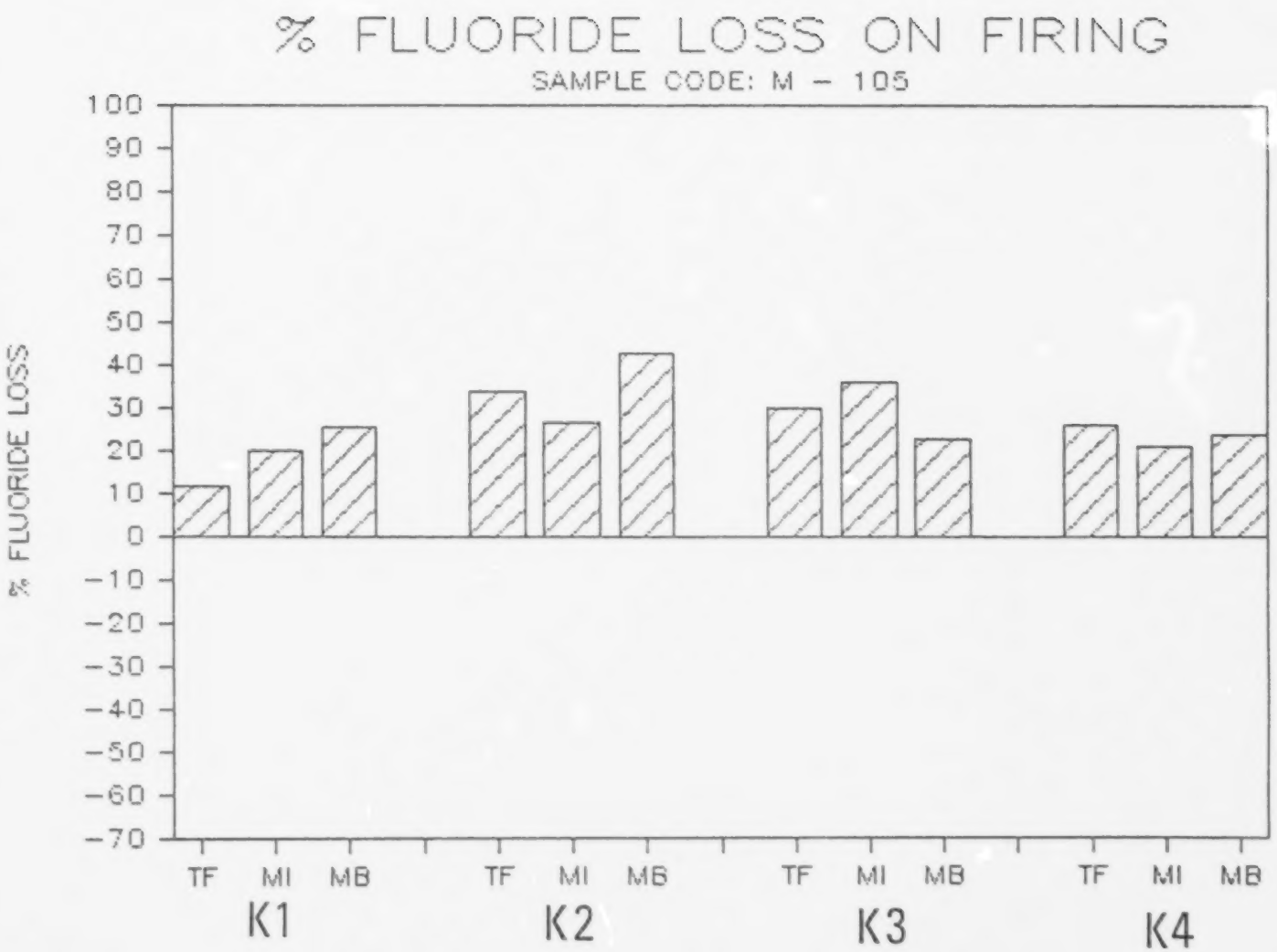
POLLUTECH


% FLUORIDE LOSS ON FIRING
SAMPLE CODE: K – 109
% FLUORIDE LOSS
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
TF MI MB TF MI MB TF MI MB TF MI MB
K1
K2
K3
K4

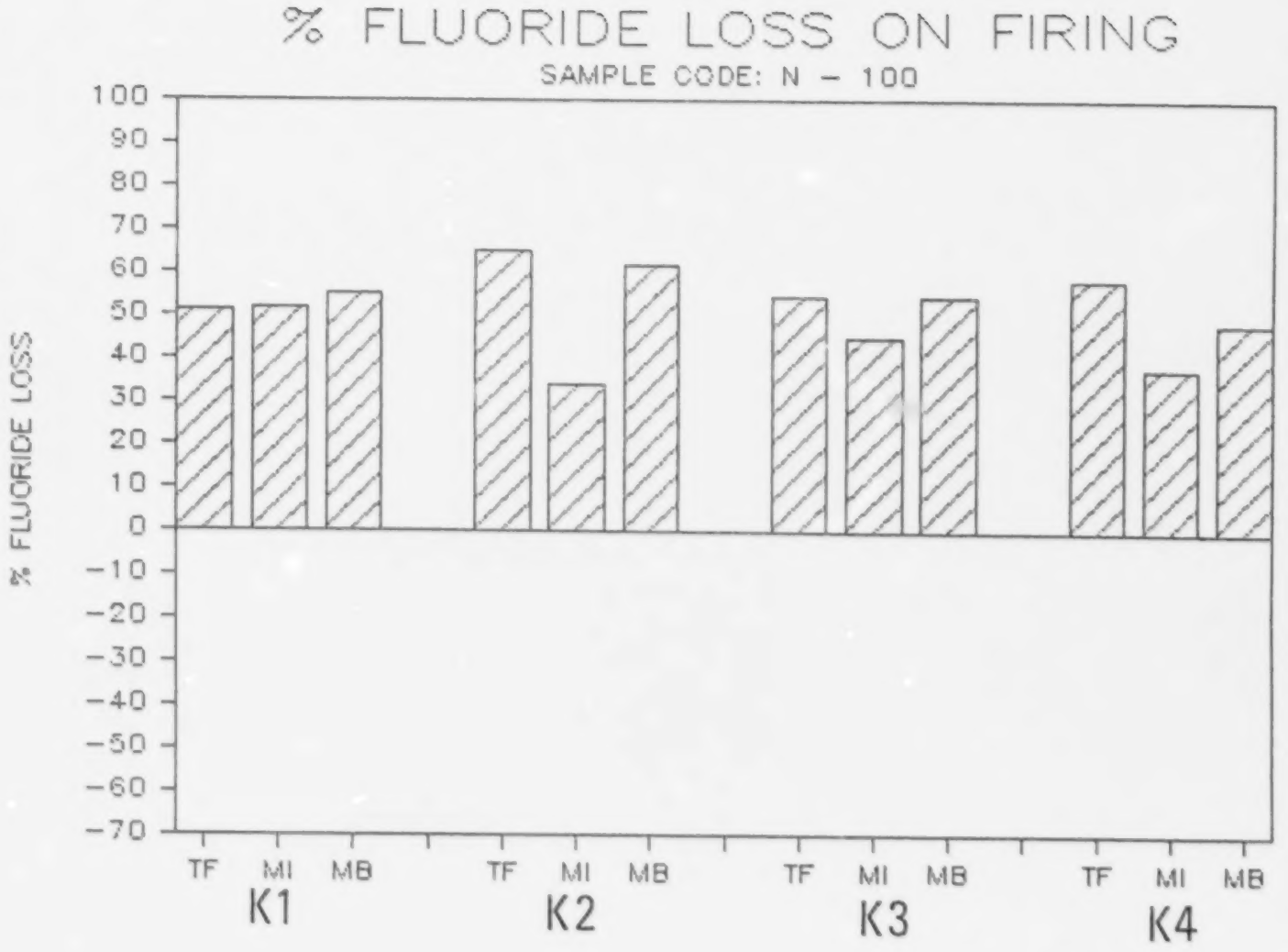
POLLUTECH


% FLUORIDE LOSS ON FIRING
SAMPLE CODE: L – XXX
% FLUORIDE LOSS
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
TF MI MB TF MI MB TF MI MB TF MI MB
K1
K2
K3
K4

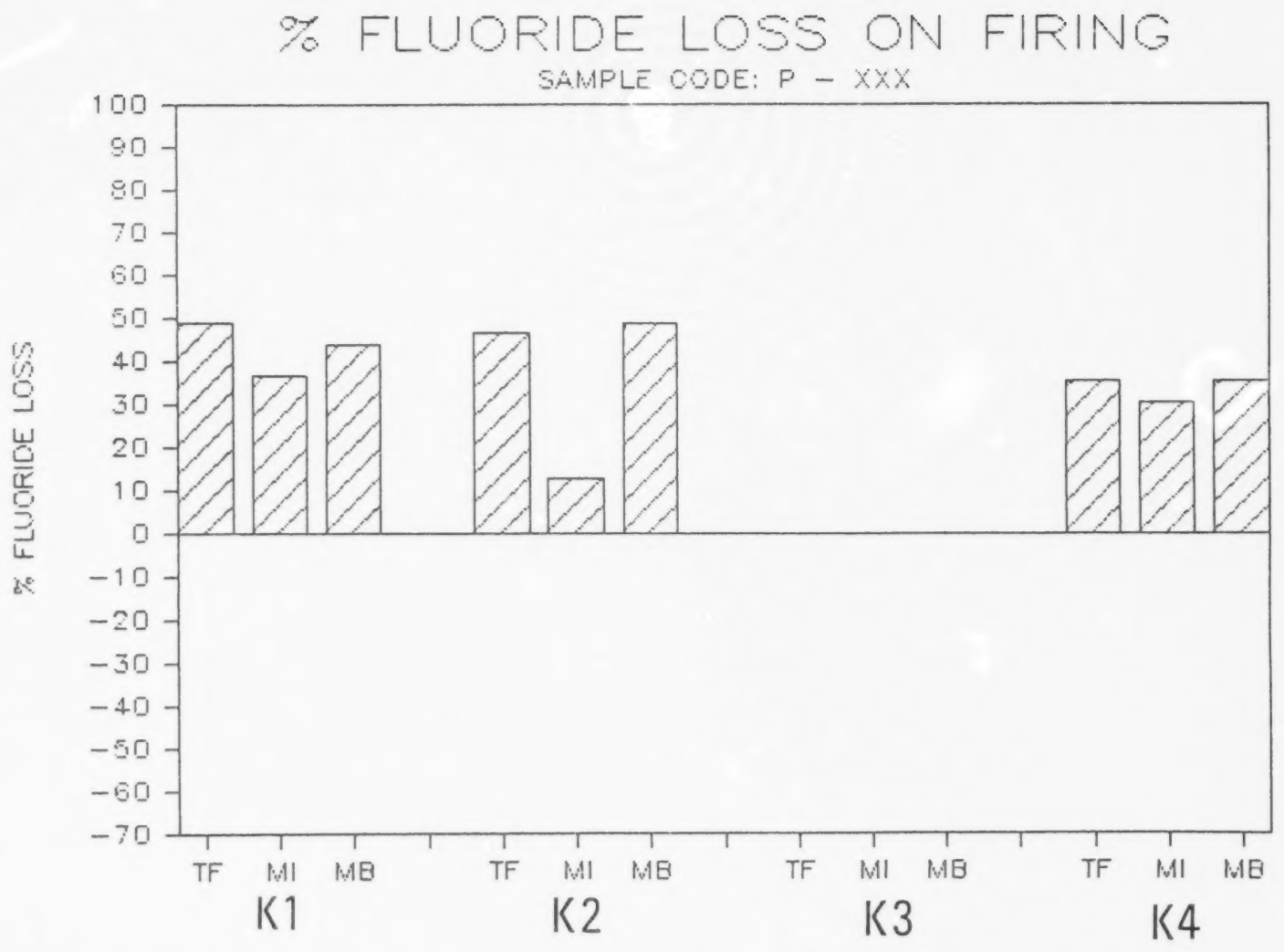
POLLUTECH


% FLUORIDE LOSS ON FIRING
SAMPLE CODE: M – 105
% FLUORIDE LOSS
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
TF MI MB
K1
TF MI MB
K2
TF MI MB
K3
TF MI MB
K4

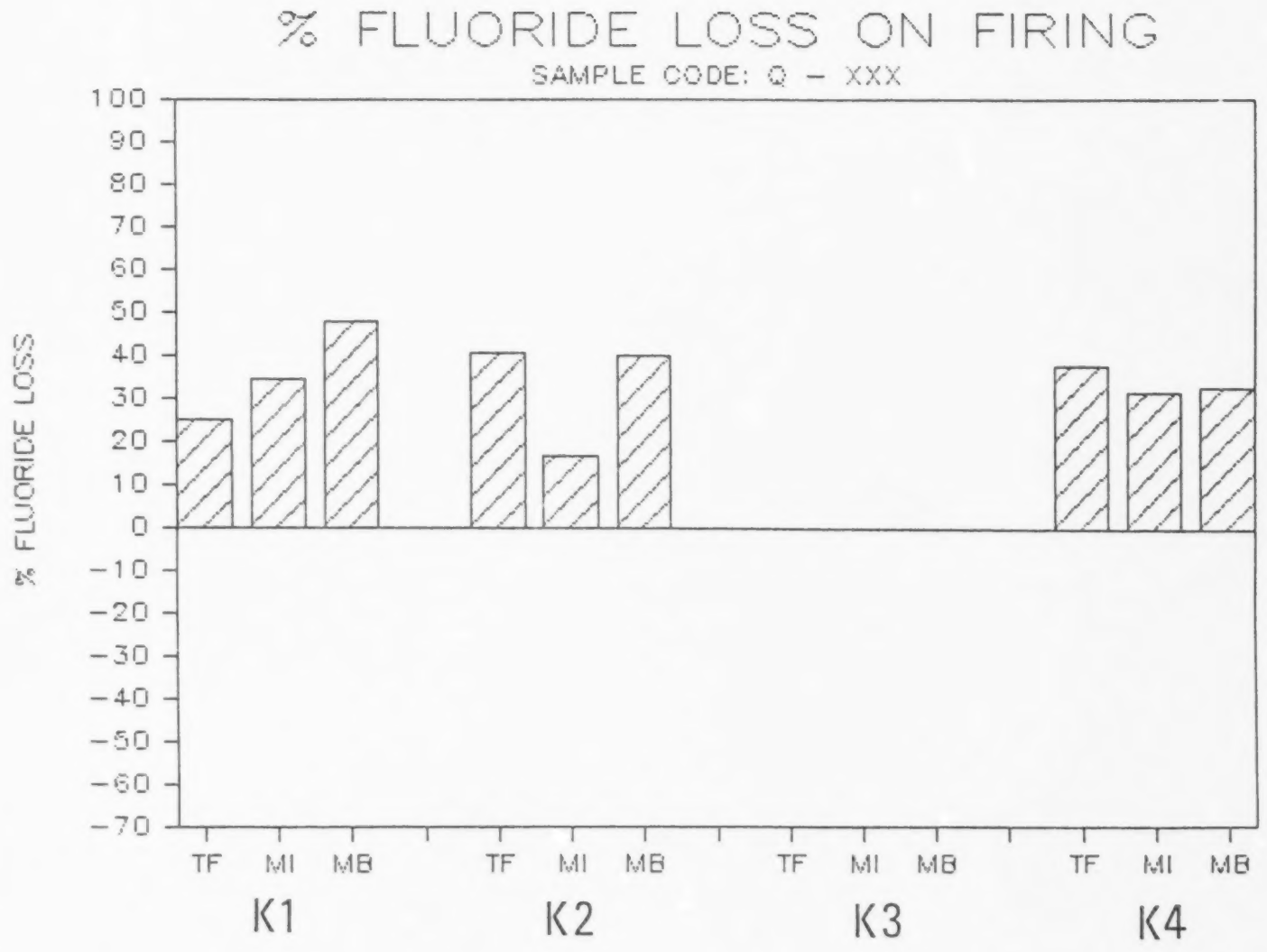
POLLUTECH


% FLUORIDE LOSS ON FIRING
SAMPLE CODE: N – 100
% FLUORIDE LOSS
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
TF MI MB
K1
TF MI MB
K2
TF MI MB
K3
TF MI MB
K4

POLLUTECH


% FLUORIDE LOSS ON FIRING
SAMPLE CODE: P – XXX
% FLUORIDE LOSS
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
TF MI MB TF MI MB TF MI MB TF MI MB
K1 K2 K3 K4

POLLUTECH


% FLUORIDE LOSS ON FIRING
SAMPLE CODE: Q – XXX
% FLUORIDE LOSS
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
TF MI MB TF MI MB TF MI MB TF MI MB
K1 K2 K3 K4

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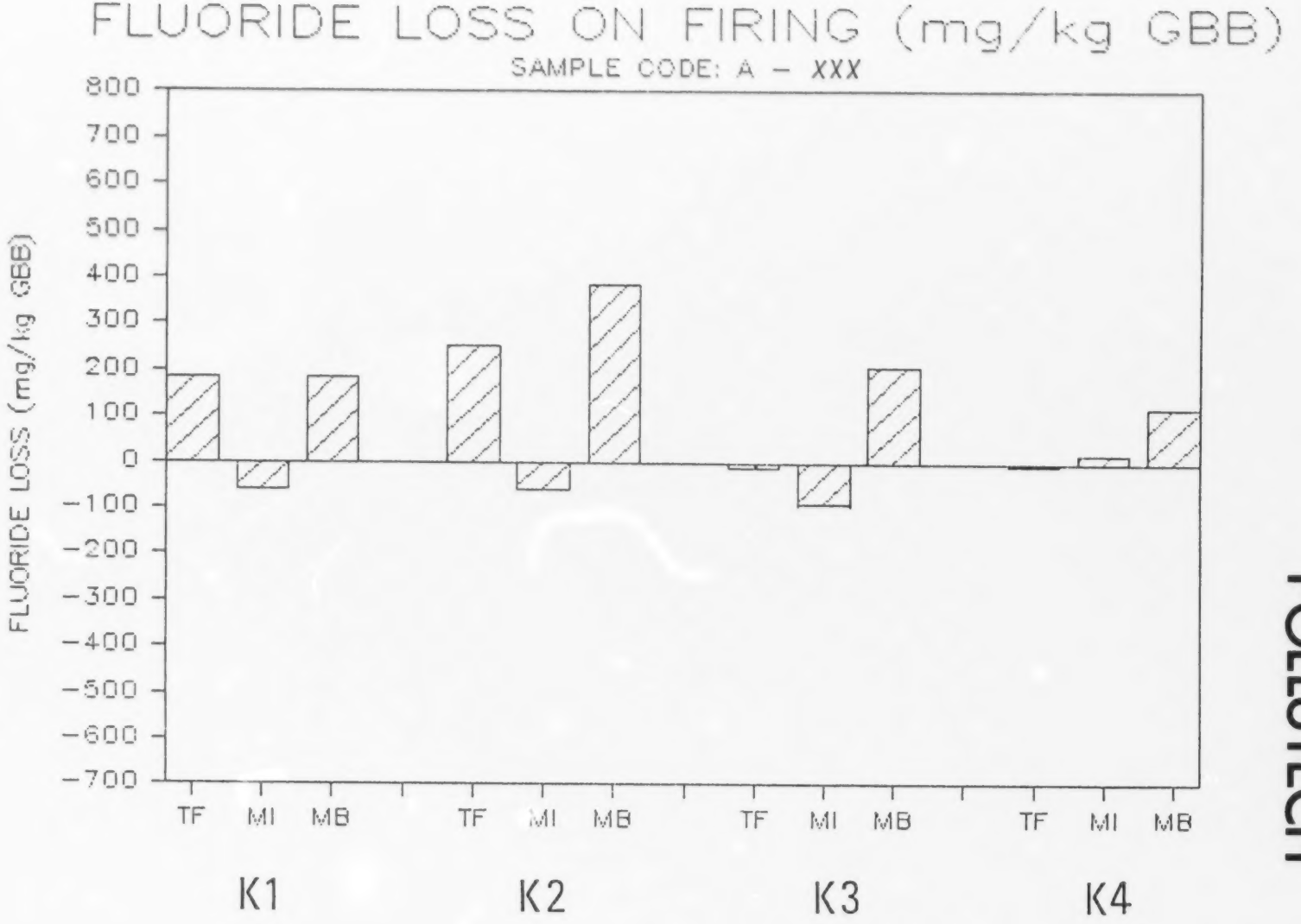
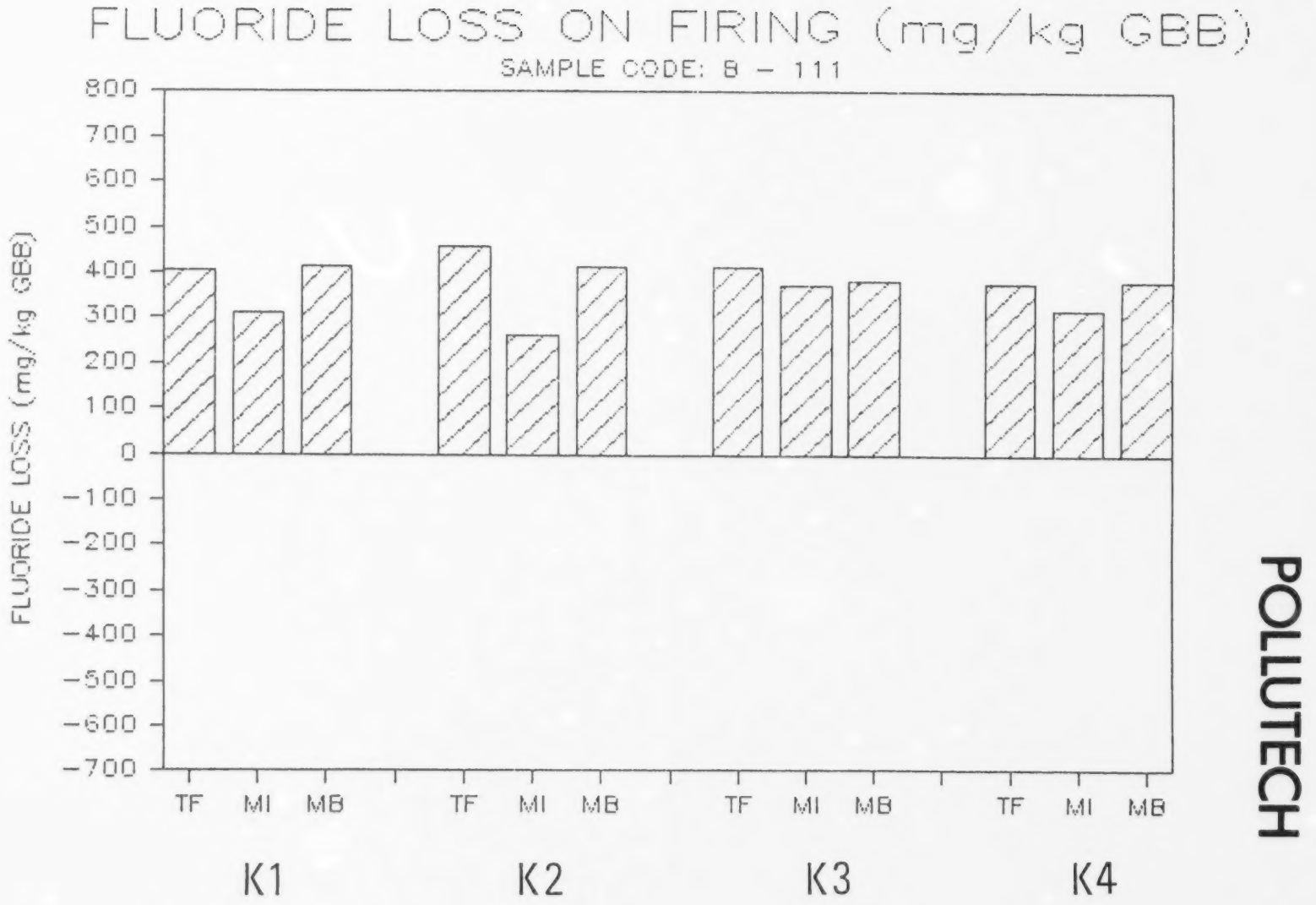
Fluoride Loss On Firing by sample

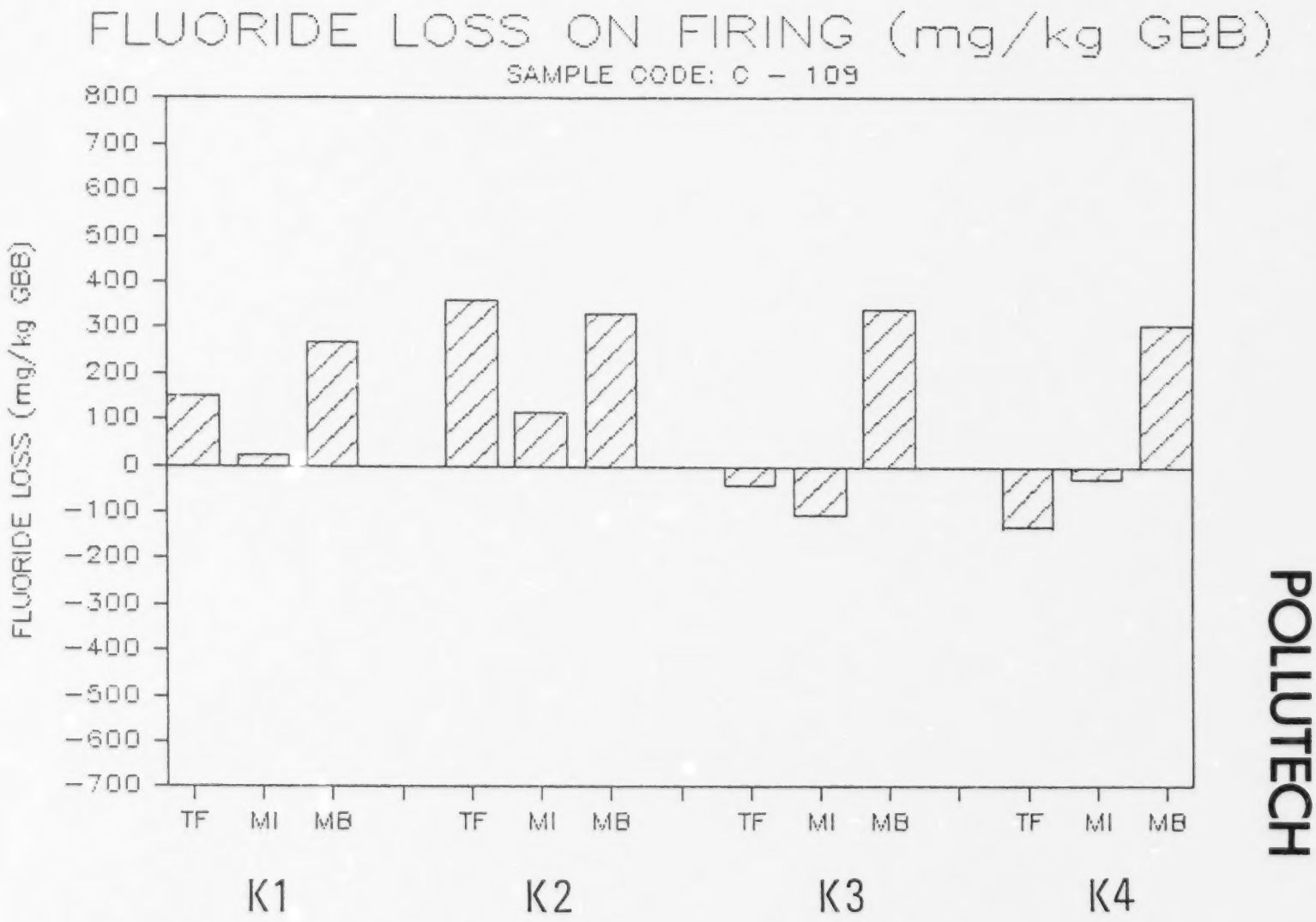
(mg/kg Green Brick Basis)


FLUORIDE LOSS ON FIRING (mg/kg GBB)
SAMPLE CODE: A – XXX
FLUORIDE LOSS (mg/kg GBB)
800
700
600
500
400
300
200
100
0
-100
-200
-300
-400
-500
-600
-700
TF
MI
MB
K1
K2
K3
K4

POLLUTECH


FLUORIDE LOSS ON FIRING (mg/kg GBB)
SAMPLE CODE: B – 111
FLUORIDE LOSS (mg/kg GBB)
800
700
600
500
400
300
200
100
0
-100
-200
-300
-400
-500
-600
-700
TF
MI
MB
K1
K2
K3
K4

POLLUTECH


FLUORIDE LOSS ON FIRING (mg/kg GBB)
SAMPLE CODE: C - 109
FLUORIDE LOSS (mg/kg GBB)
800
700
600
500
400
300
200
100
0
-100
-200
-300
-400
-500
-600
-700
TF MI MB TF MI MB TF MI MB TF MI MB
K1
K2
K3
K4

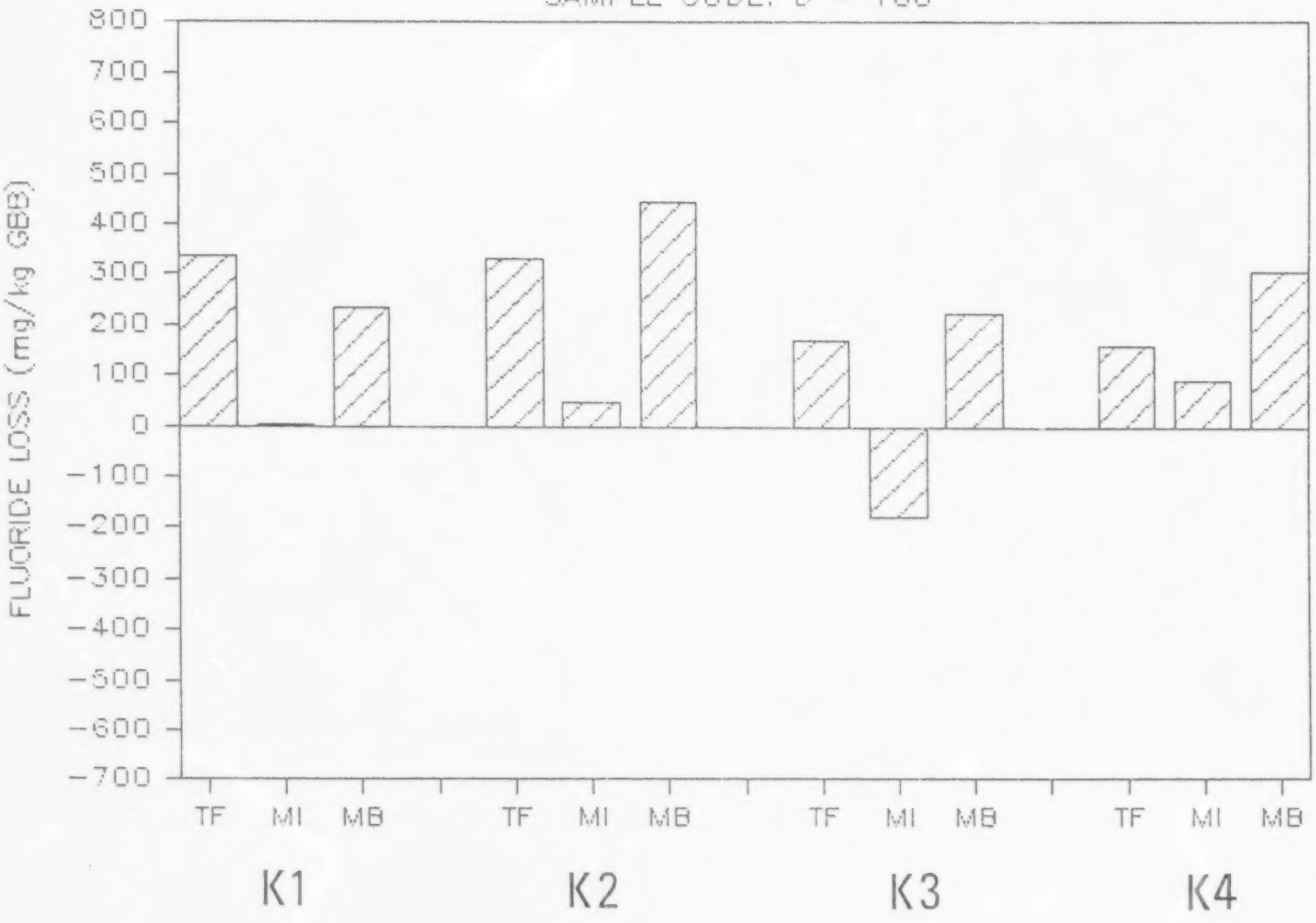
POLLUTECH

FLUORIDE LOSS ON FIRING (mg/kg GBB)
SAMPLE CODE: D - 108
FLUORIDE LOSS (mg/kg GBB)
800
700
600
500
400
300
200
100
0
-100
-200
-300
-400
-500
-600
-700
TF MI MB TF MI MB TF MI MB TF MI MB
K1 K2 K3 K4

POLLUTECH

FLUORIDE LOSS ON FIRING (mg/kg GBB)

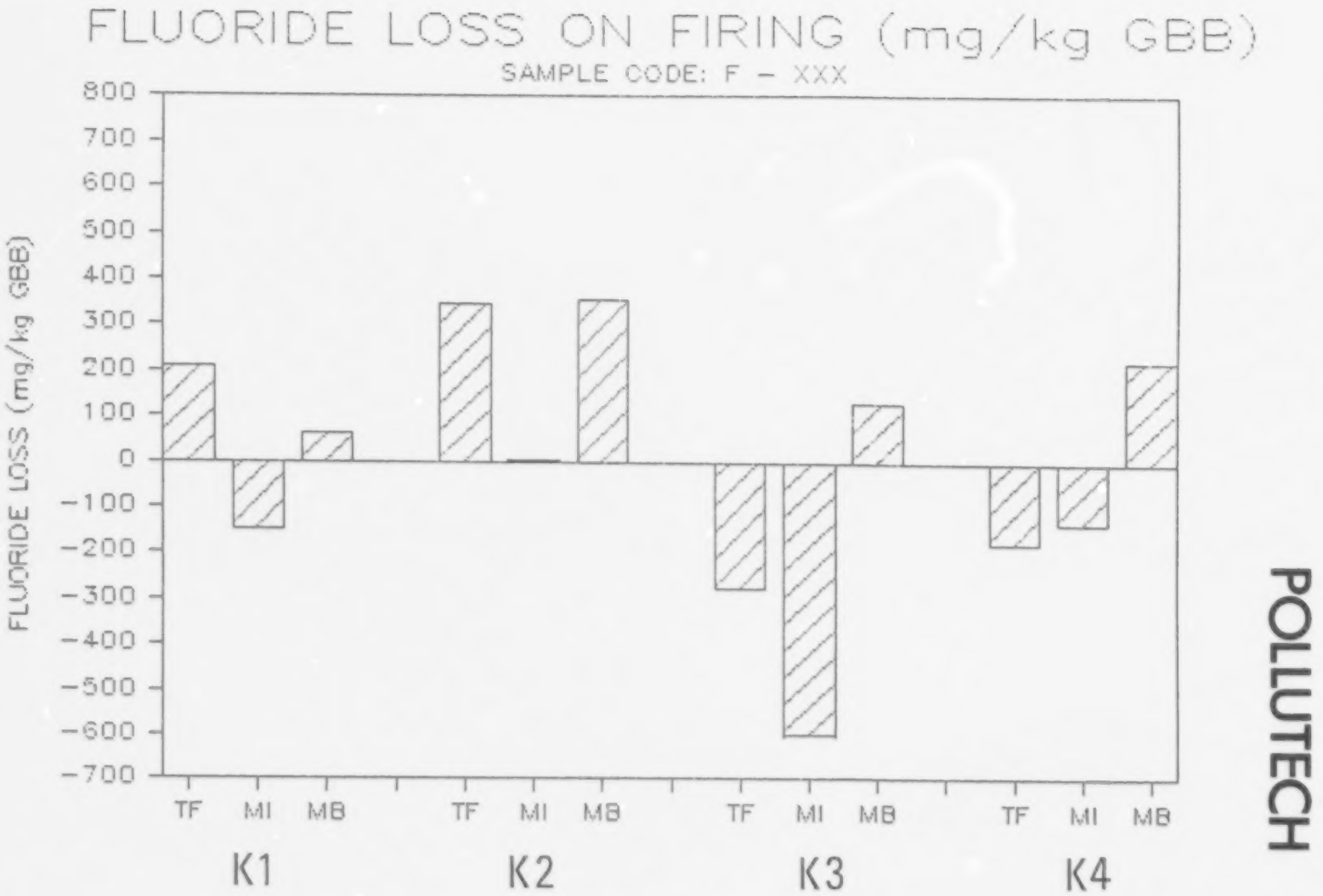
SAMPLE CODE: 0"- 108



POLLUTECH

FLUORIDE LOSS ON FIRING (mg/kg GBB)
SAMPLE CODE: E – 103
FLUORIDE LOSS (mg/kg GBB)
800
700
600
500
400
300
200
100
0
−100
−200
−300
−400
−500
−600
−700
TF MI MB TF MI MB TF MI MB TF MI MB
K1
K2
K3
K4

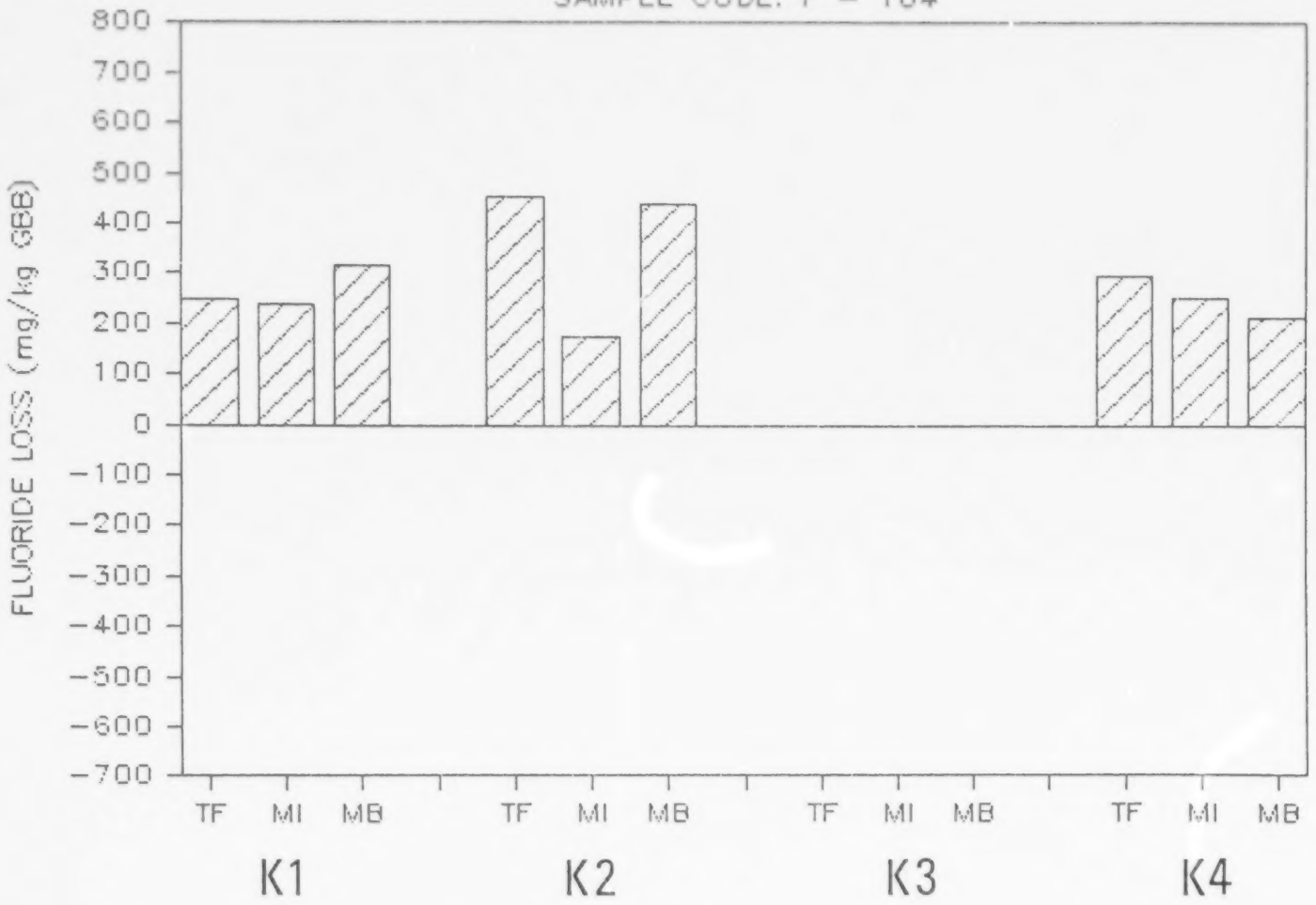
POLLUTECH


FLUORIDE LOSS ON FIRING (mg/kg GBB)
SAMPLE CODE: F – XXX
FLUORIDE LOSS (mg/kg GBB)
800
700
600
500
400
300
200
100
0
−100
−200
−300
−400
−500
−600
−700
TF MI MB TF MI MB TF MI MB TF MI MB
K1
K2
K3
K4

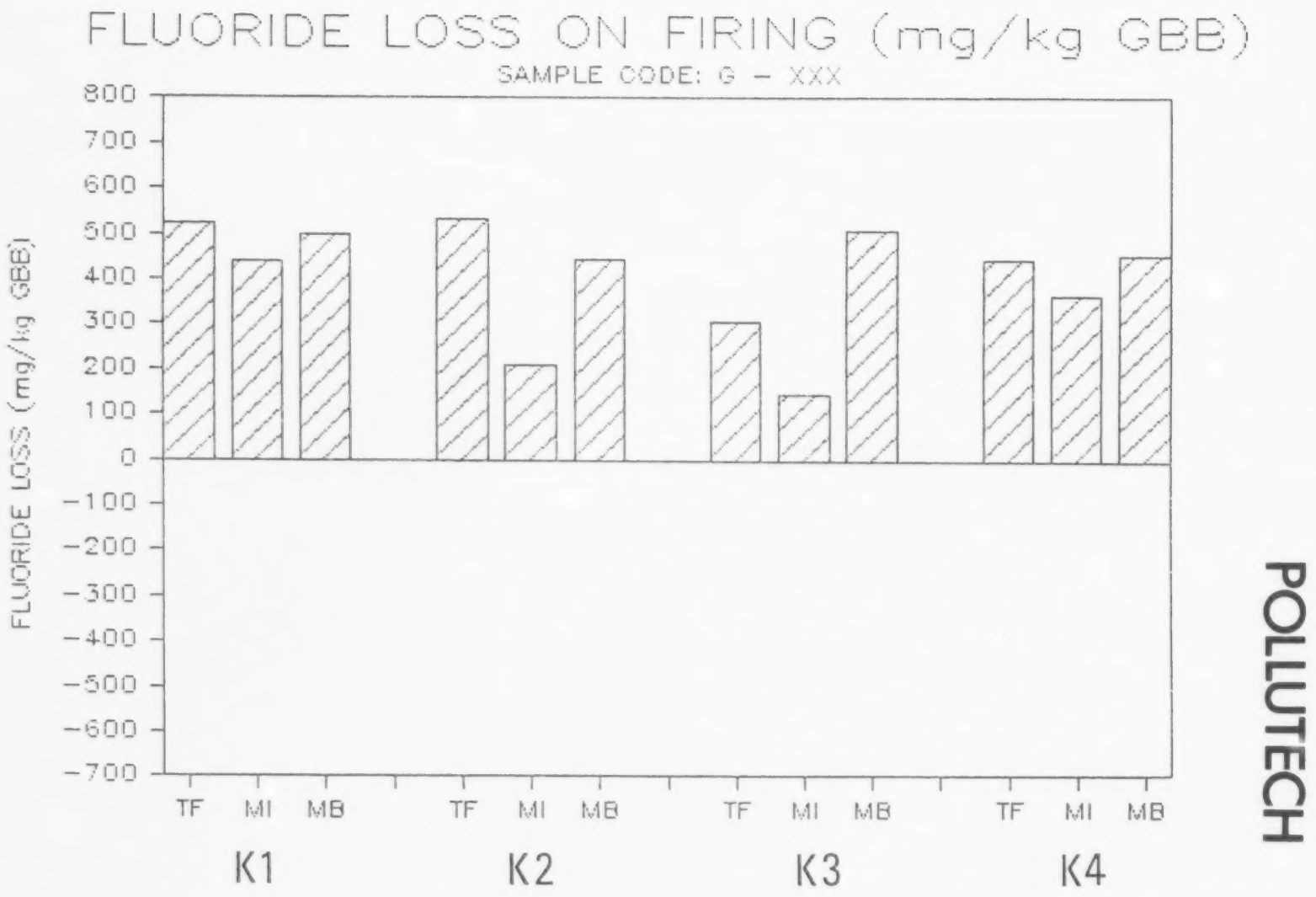
POLLUTECH

FLUORIDE LOSS ON FIRING (mg/kg GBB)

SAMPLE CODE: F"- 104



POLLUTECH


FLUORIDE LOSS ON FIRING (mg/kg GBB)
SAMPLE CODE: G - XXX
FLUORIDE LOSS (mg/kg GBB)
800
700
600
500
400
300
200
100
0
-100
-200
-300
-400
-500
-600
-700
TF MI MB TF MI MB TF MI MB TF MI MB
K1 K2 K3 K4

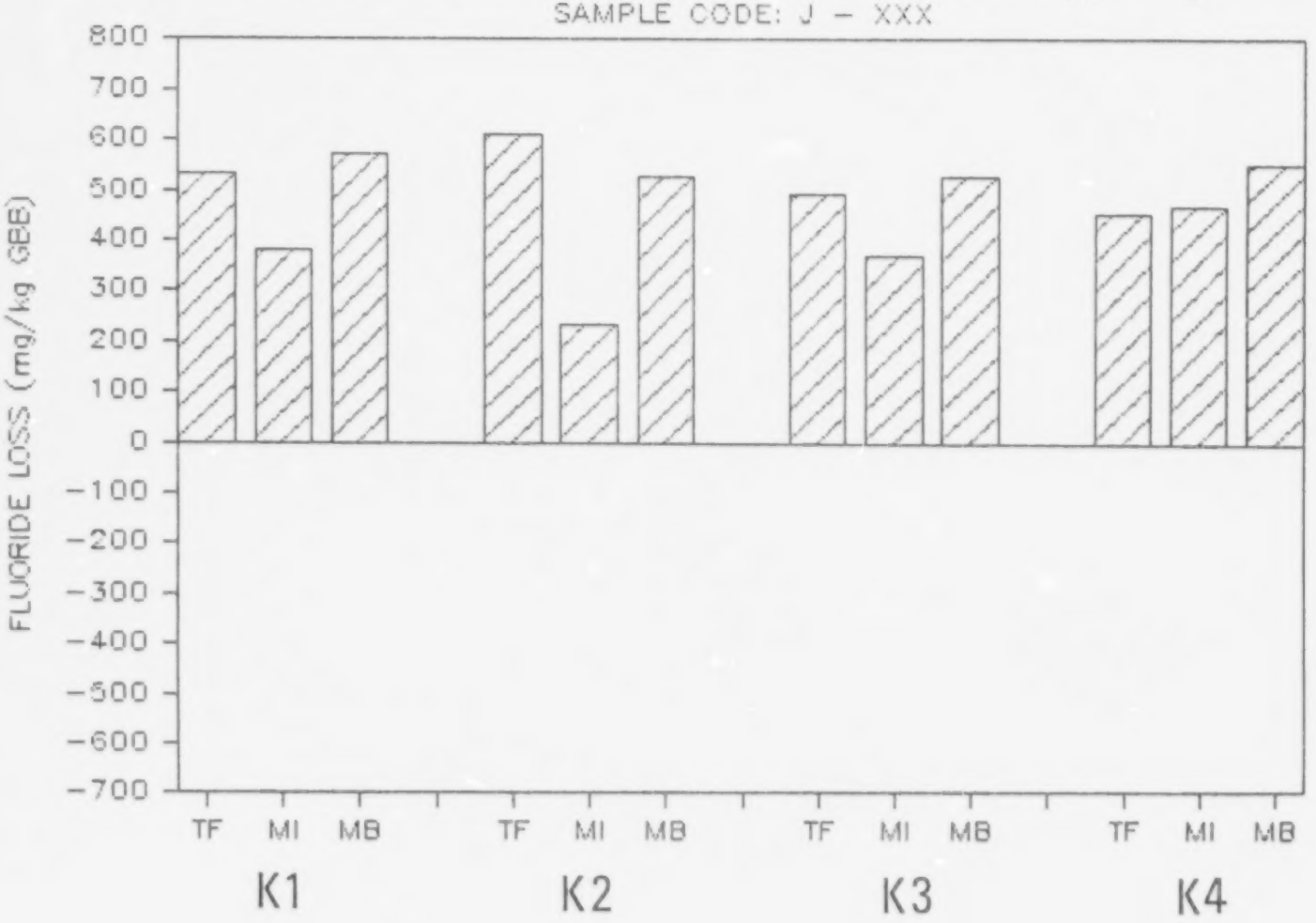
POLLUTECH

FLUORIDE LOSS ON FIRING (mg/kg GBB)
SAMPLE CODE: H - 107
FLUORIDE LOSS (mg/kg GBB)
800
700
600
500
400
300
200
100
0
-100
-200
-300
-400
-500
-600
-700
TF MI MB TF MI MB TF MI MB TF MI MB
K1 K2 K3 K4

POLLUTECH

FLUORIDE LOSS ON FIRING (mg/kg GBB)

SAMPLE CODE: J – XXX



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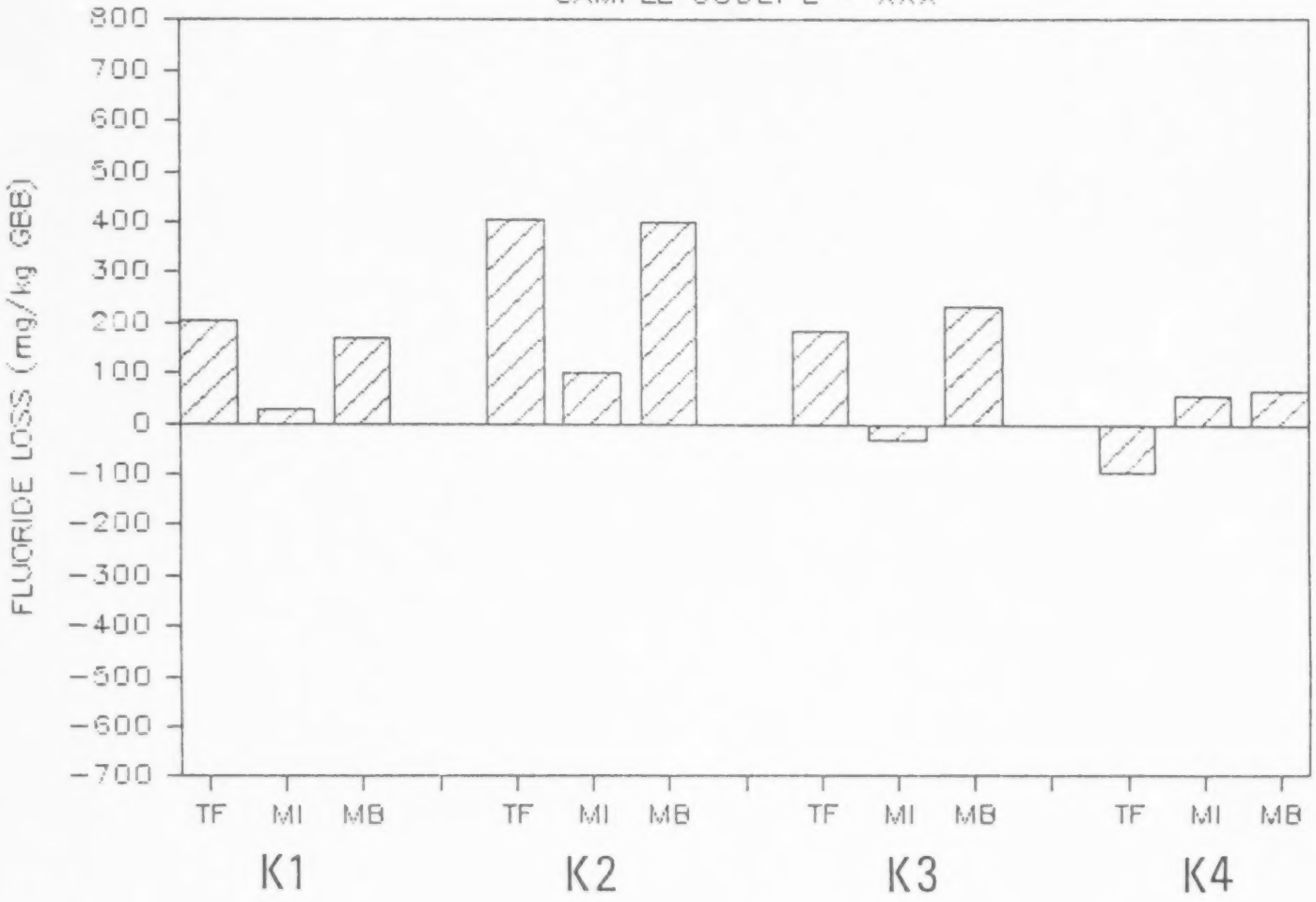
FLUORIDE LOSS ON FIRING (mg/kg GBB)
SAMPLE CODE: K – 109
FLUORIDE LOSS (mg/kg GBB)
800
700
600
500
400
300
200
100
0
-100
-200
-300
-400
-500
-600
-700
TF
MI
MB
K1
K2
K3
K4

POLLUTECH

FLUORIDE LOSS ON FIRING (mg/kg GBB)

SAMPLE CODE: L - XXX



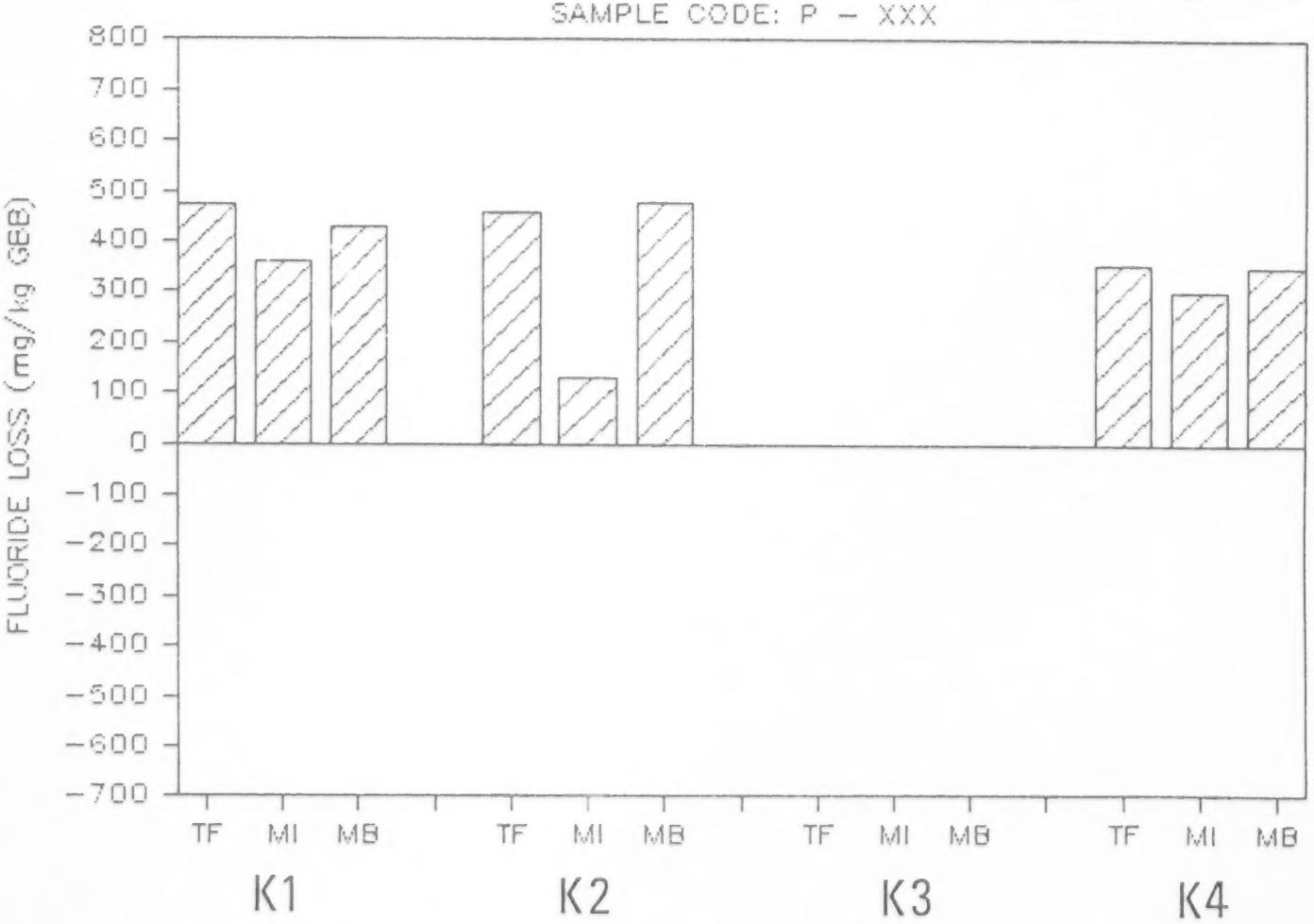
POLLUTECH

FLUORIDE LOSS ON FIRING (mg/kg GBB)
SAMPLE CODE: M - 105
FLUORIDE LOSS (mg/kg GBB)
800
700
600
500
400
300
200
100
0
-100
-200
-300
-400
-500
-600
-700
TF MI MB TF MI MB TF MI MB TF MI MB
K1 K2 K3 K4
POLLUTECH

FLUORIDE LOSS ON FIRING (mg/kg GBB)
SAMPLE CODE: N - 100
FLUORIDE LOSS (mg/kg GBB)
800
700
600
500
400
300
200
100
0
-100
-200
-300
-400
-500
-600
-700
TF MI MB TF MI MB TF MI MB TF MI MB
K1 K2 K3 K4

POLLUTECH

FLUORIDE LOSS ON FIRING (mg/kg GBB)



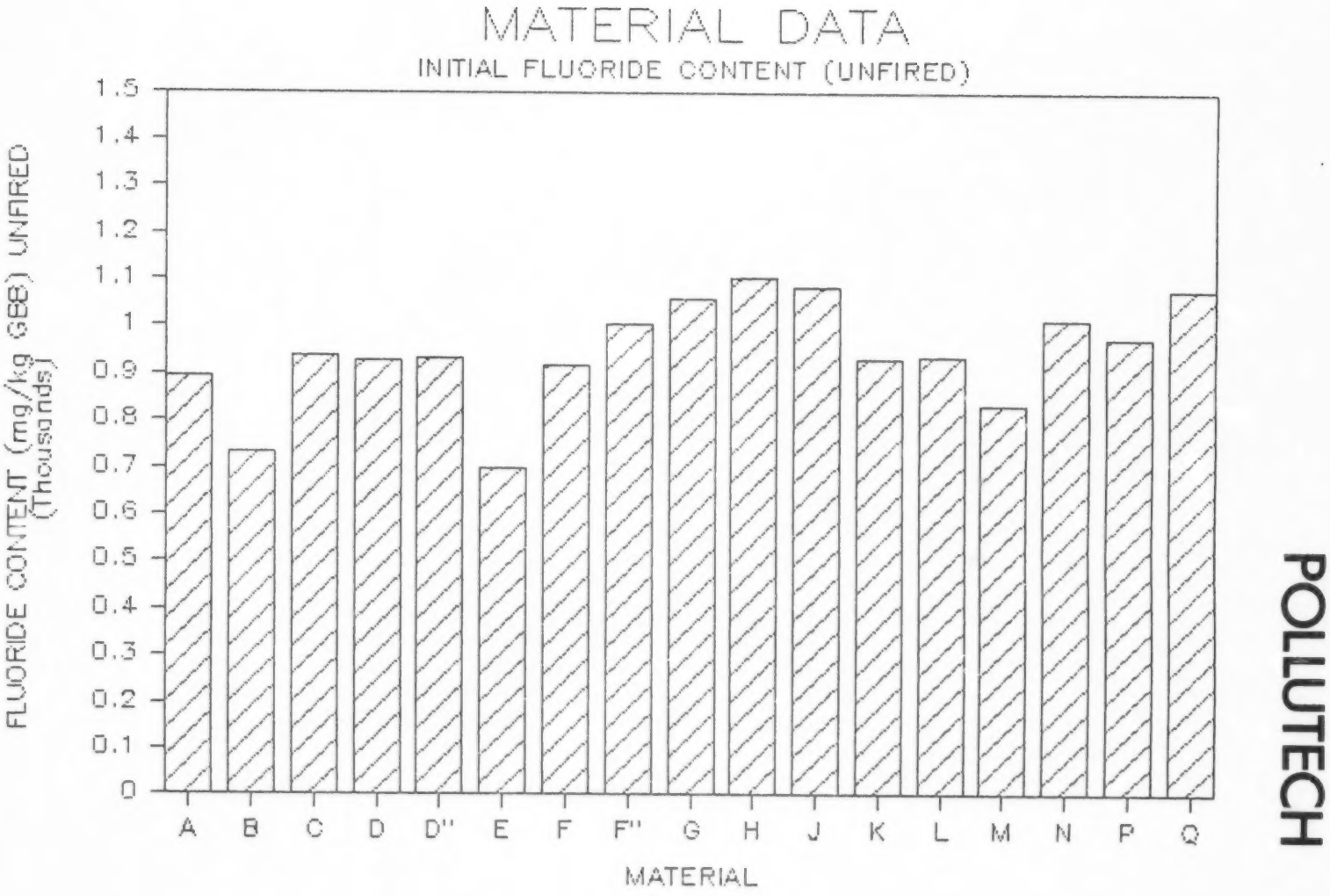
POLLUTECH

FLUORIDE LOSS ON FIRING (mg/kg GBB)
SAMPLE CODE: Q - XXX
FLUORIDE LOSS (mg/kg GBB)
800
700
600
500
400
300
200
100
0
-100
-200
-300
-400
-500
-600
-700
TF
MI
MB
K1
K2
K3
K4

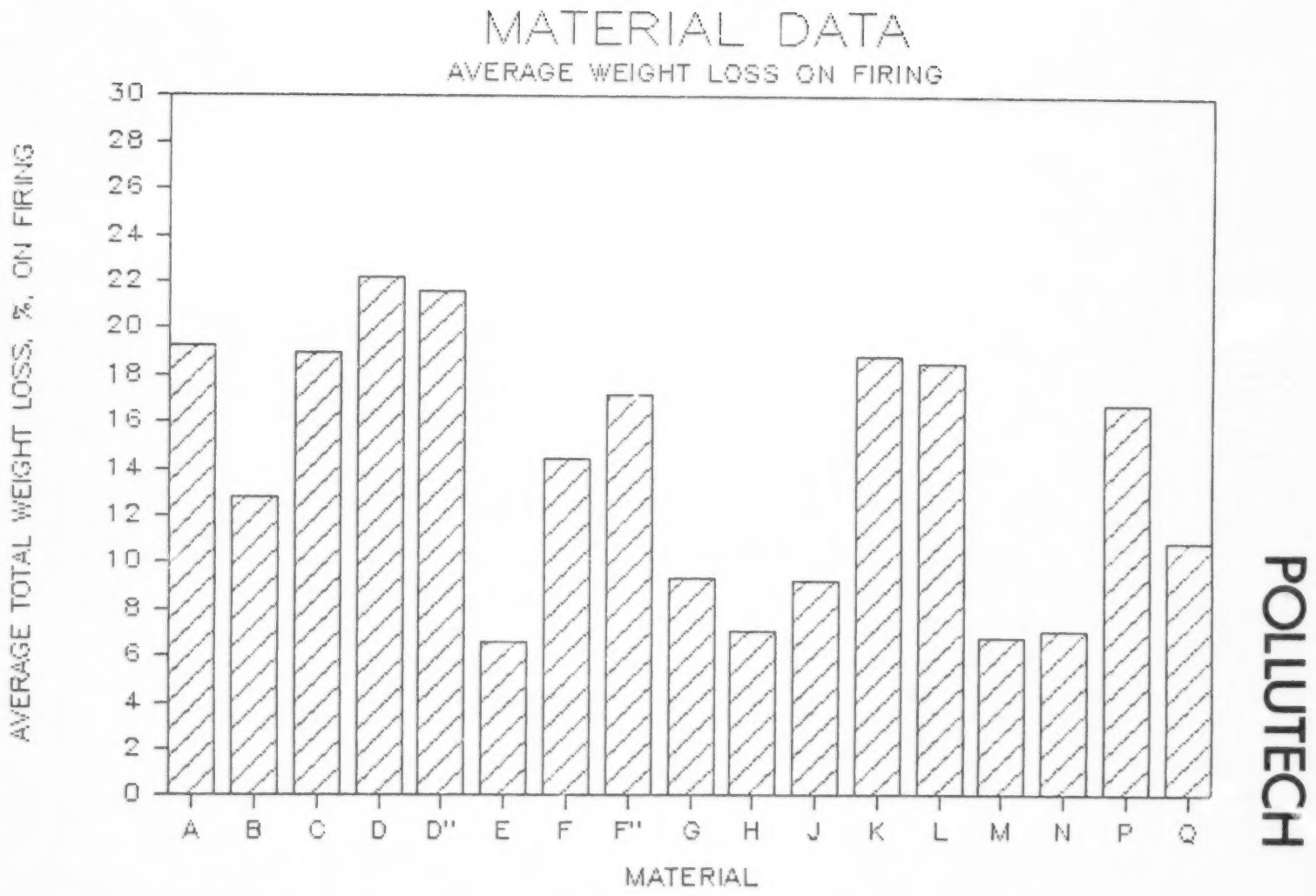
POLLUTECH

POLLUTECH

Material Data


MATERIAL DATA
INITIAL FLUORIDE CONTENT (UNFIRED)
FLUORIDE CONTENT (mg/kg GBB) UNFIRED
(Thousands)
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
A
B
C
D
D''
E
F
F''
G
H
J
K
L
M
N
P
Q
MATERIAL

POLLUTECH


MATERIAL DATA
AVERAGE WEIGHT LOSS ON FIRING
AVERAGE TOTAL WEIGHT LOSS, %, ON FIRING
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
A
B
C
D
D''
E
F
F''
G
H
J
K
L
M
N
P
Q
MATERIAL

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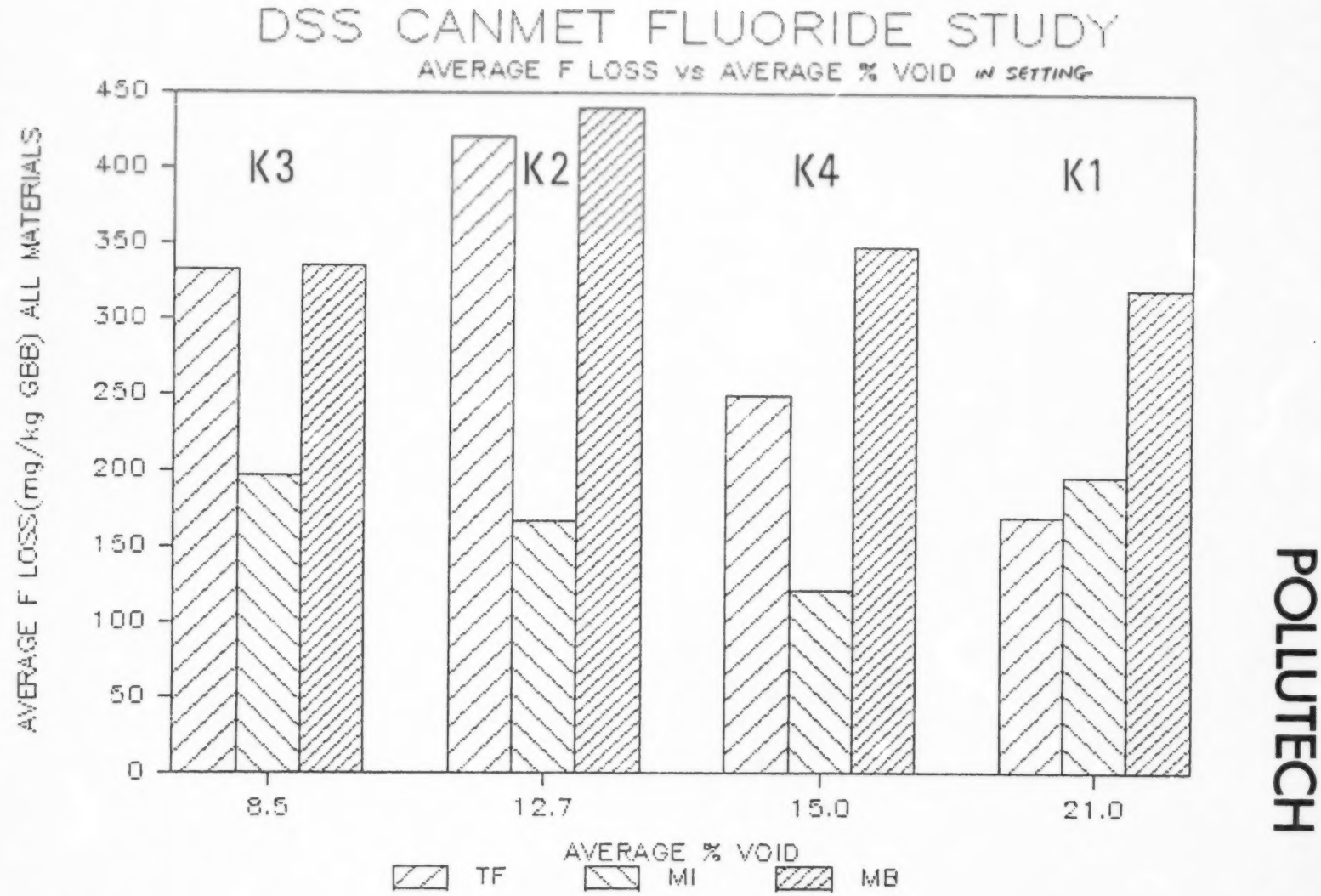
Average F Loss vs Average % Void in Settling


DSS CANMET FLUORIDE STUDY
AVERAGE F LOSS vs AVERAGE % VOID IN SETTING
AVERAGE F LOSS(mg/kg GEB) ALL MATERIALS
450
400
350
300
250
200
150
100
50
0
K3
K2
K4
K1
8.5
12.7
15.0
21.0
AVERAGE % VOID
TF
MI
MB

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Fluoride Loss On Firing
vs Position Along Car

A-G = lst Car

H-N/Q = 2nd Car

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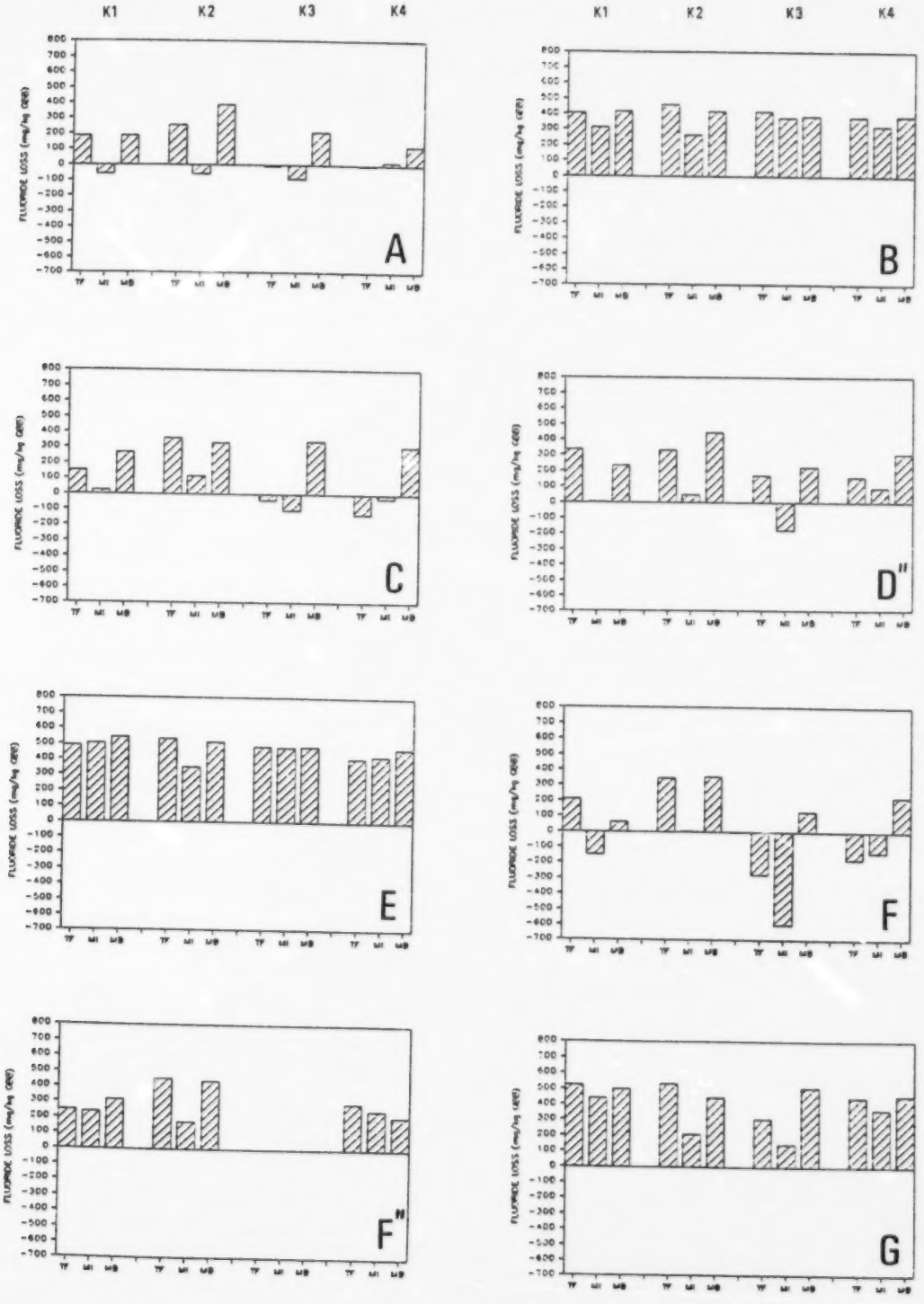
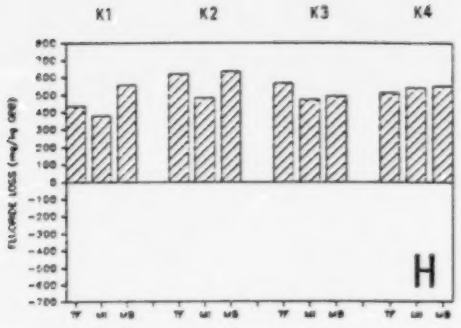
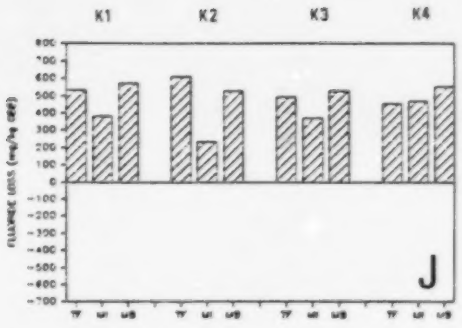
F LOSS ON FIRING vs CAR POSITIONS

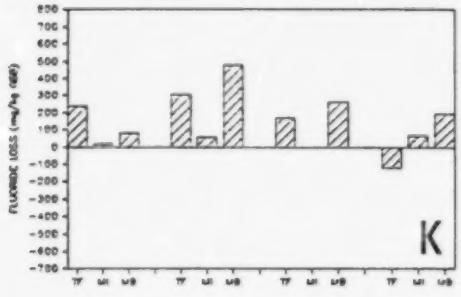


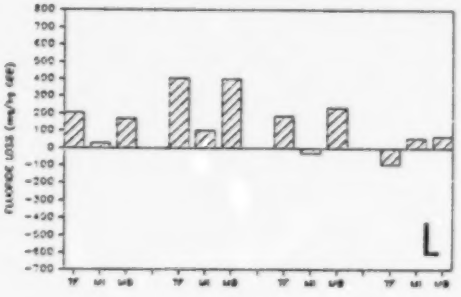
POLLUTECH

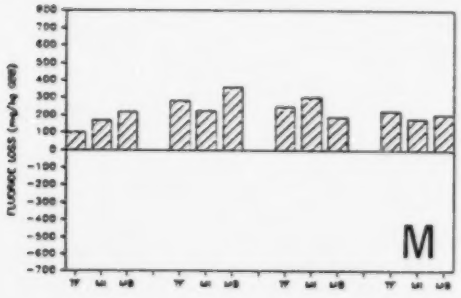
F LOSS ON FIRING vs CAR POSITIONS

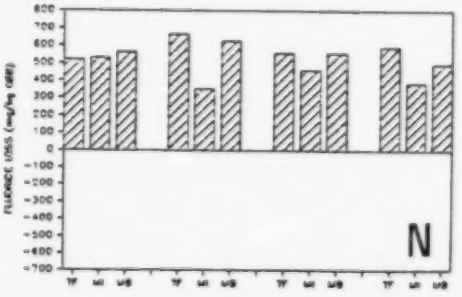


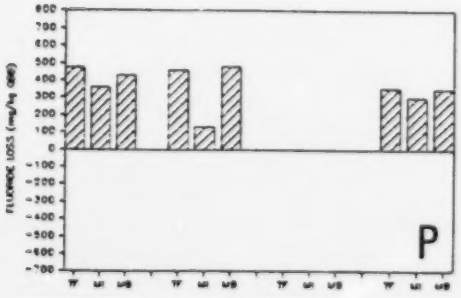


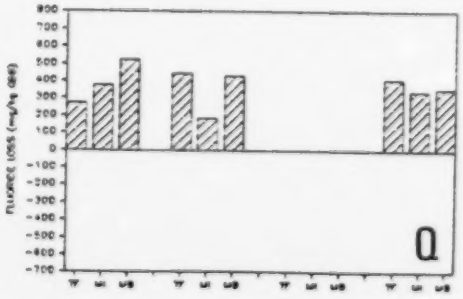












9. APPENDICES

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APPENDIX 1

References

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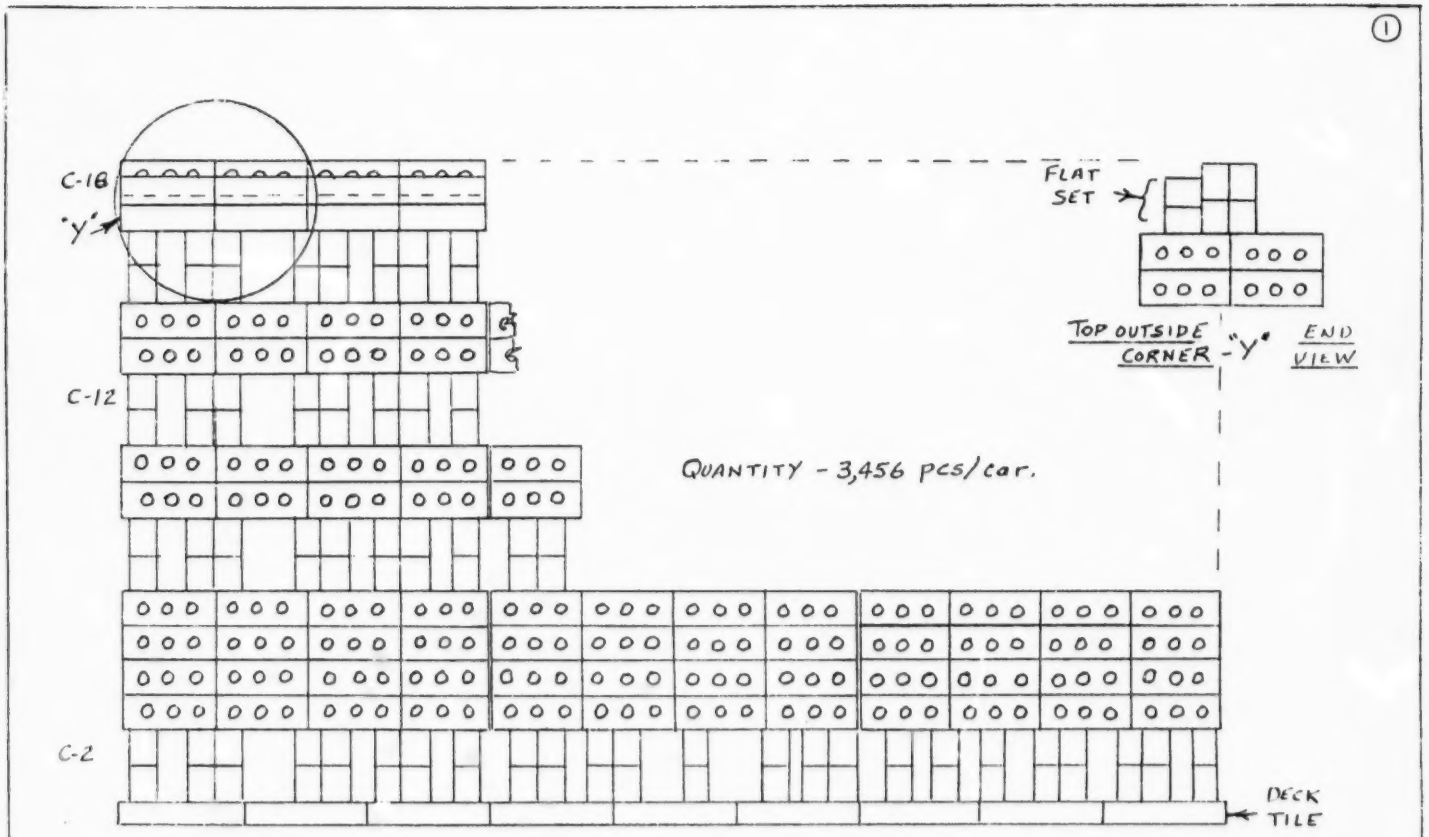
APPENDIX 2

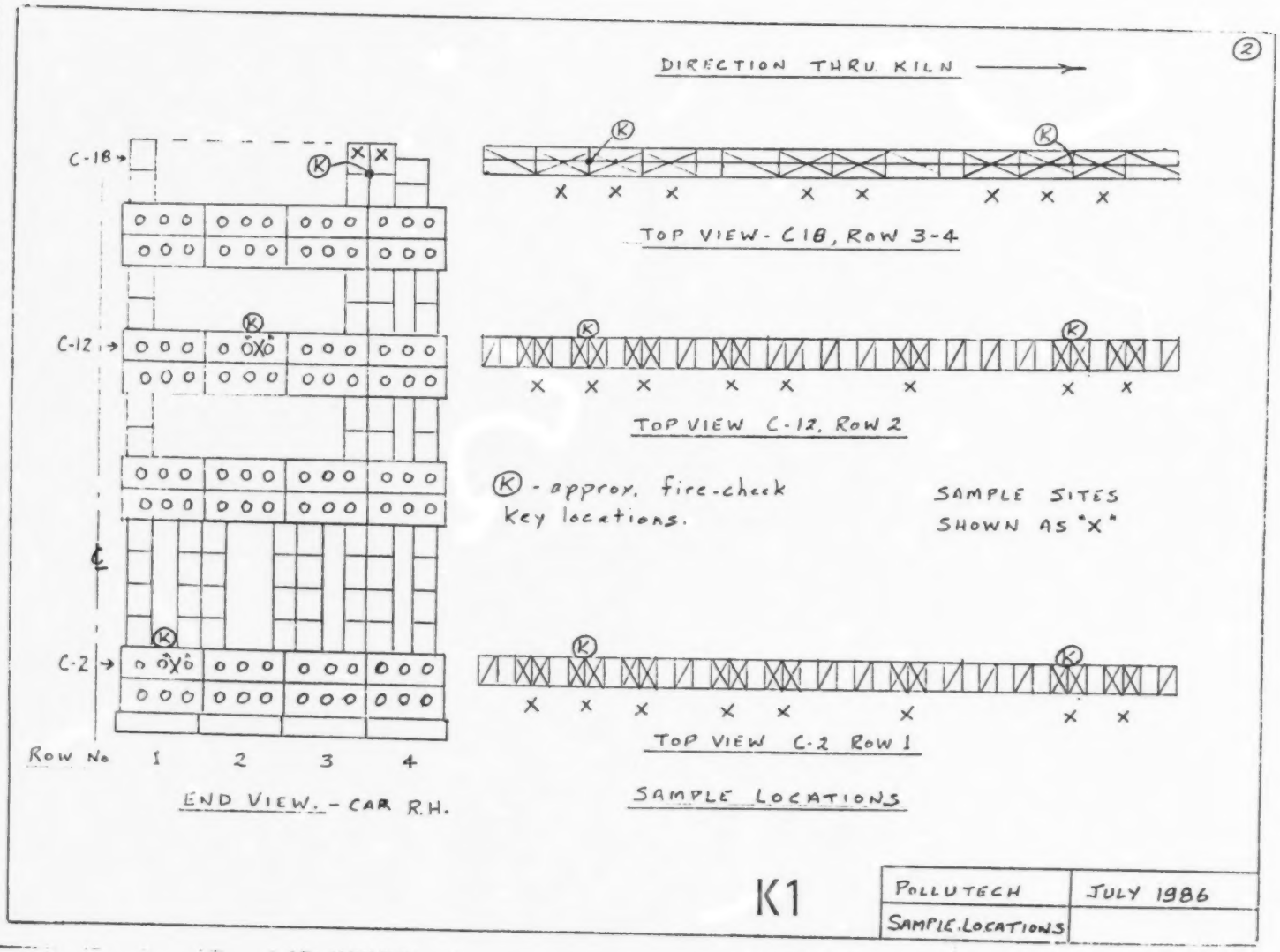
Kiln Car Settings



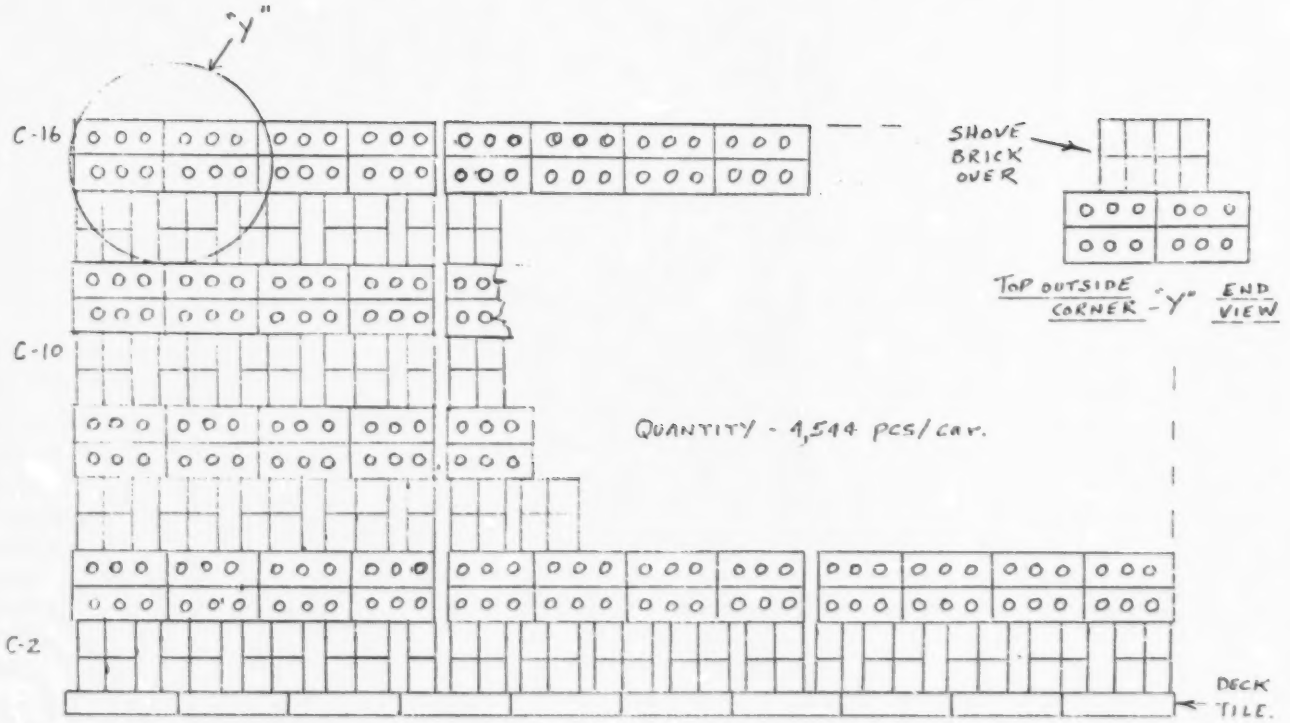
K1

POLLUTECH	JULY 1986
CAR SETTING	

POLLUTECH


②
DIRECTION THRU KILN
C-18
C-12
C-2
Row No 1 2 3 4
END VIEW. - CAR R.H.
TOP VIEW - C18, ROW 3-4
TOP VIEW C-12, ROW 2
TOP VIEW C-2 ROW 1
Ⓚ - approx. fire-check key locations.
SAMPLE SITES SHOWN AS "X"
SAMPLE LOCATIONS
K1
POLLUTECH
JULY 1986
SAMPLE LOCATIONS

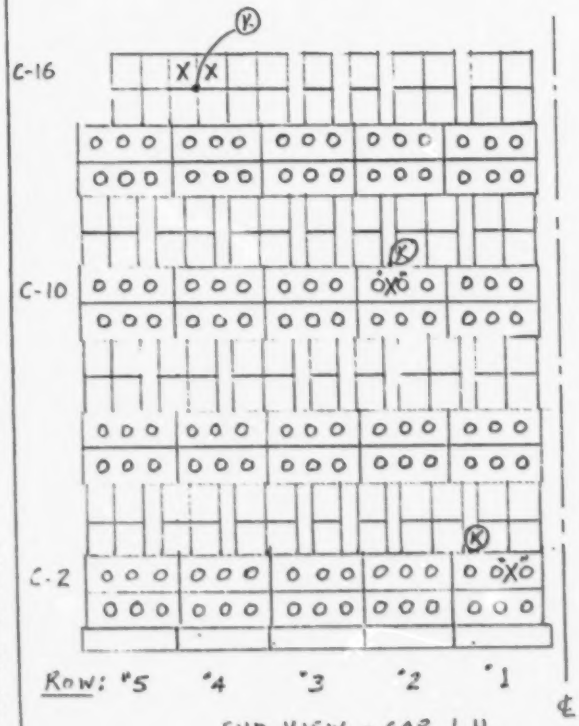
POLLUTECH



K2

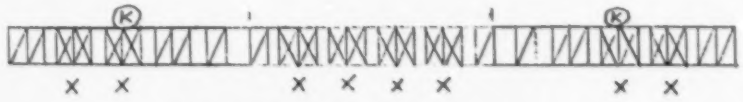
POLLUTECH	JULY 1986
CAR SETTING	

POLLUTECH



END VIEW. - CAR L.H.

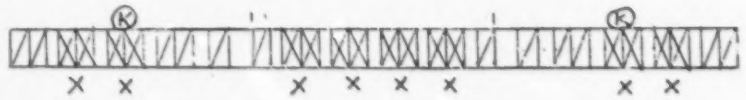
TOP VIEW C-16, ROW 4



TOP VIEW C-10, ROW 2.

Ⓚ - approx. fire-check key locations.

SAMPLE SITES SHOWN AS 'X'



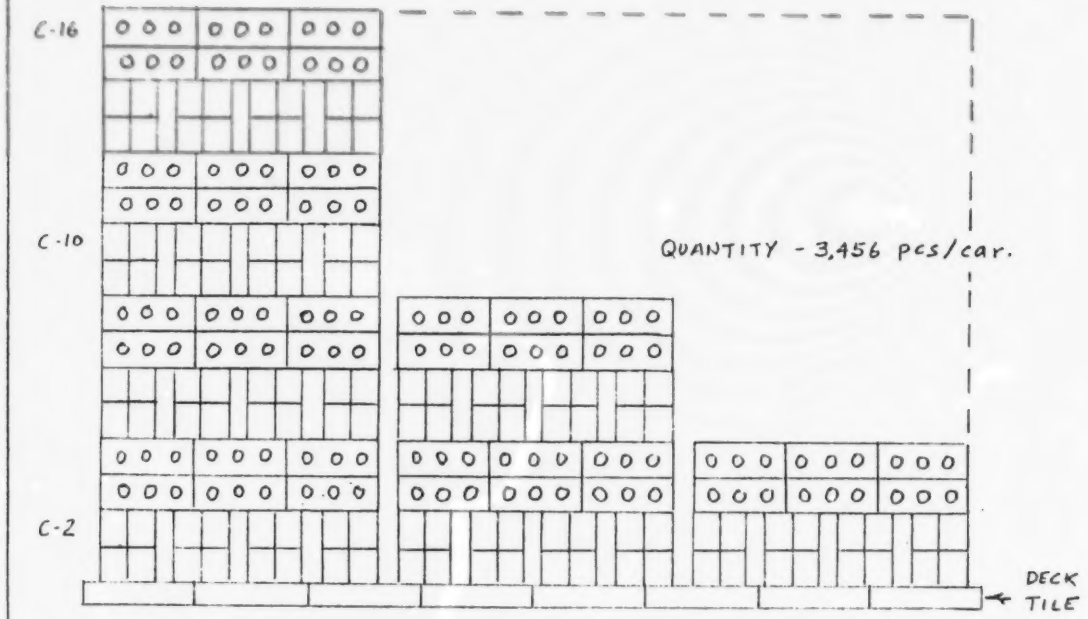
TOP VIEW C-2, ROW 1.

SAMPLE LOCATIONS.

K2

POLLUTECH	JULY 1986
SAMPLE LOCATIONS	

POLLUTECH

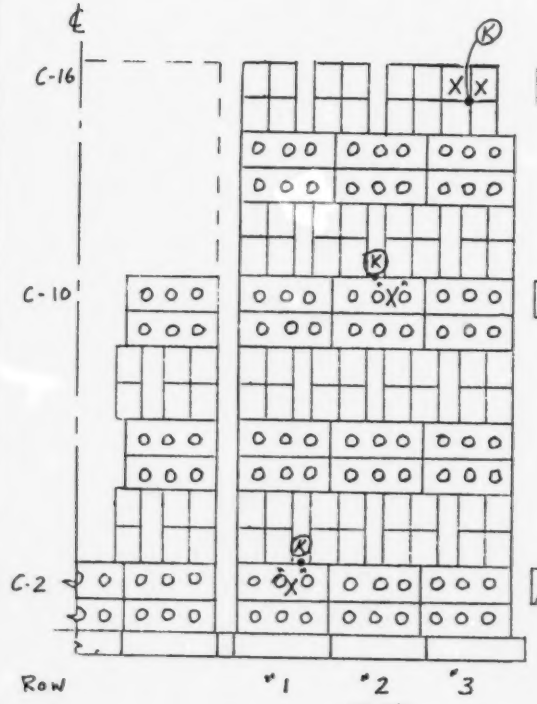


SIDE VIEW. - C.S.R. SIZE.

K3

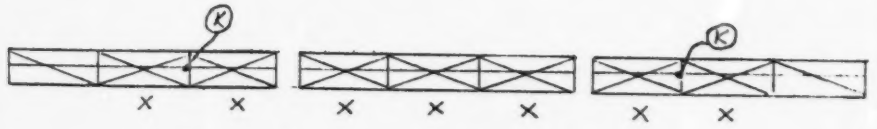
POLLUTECH	JULY 1986
CAR SETTING	

POLLUTECH

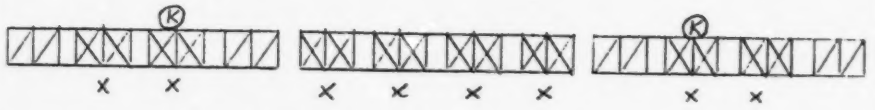


END VIEW. - CAR R.H

Note: 9 brick wide in 3 hacks.



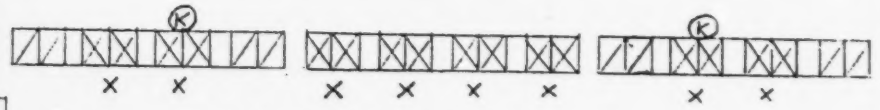
TOP VIEW C-16, ROW 3 OUTSIDE



TOP VIEW C10, ROW 2

(K) - approx fire-check key locations

SAMPLE SITES SHOWN AS 'X'



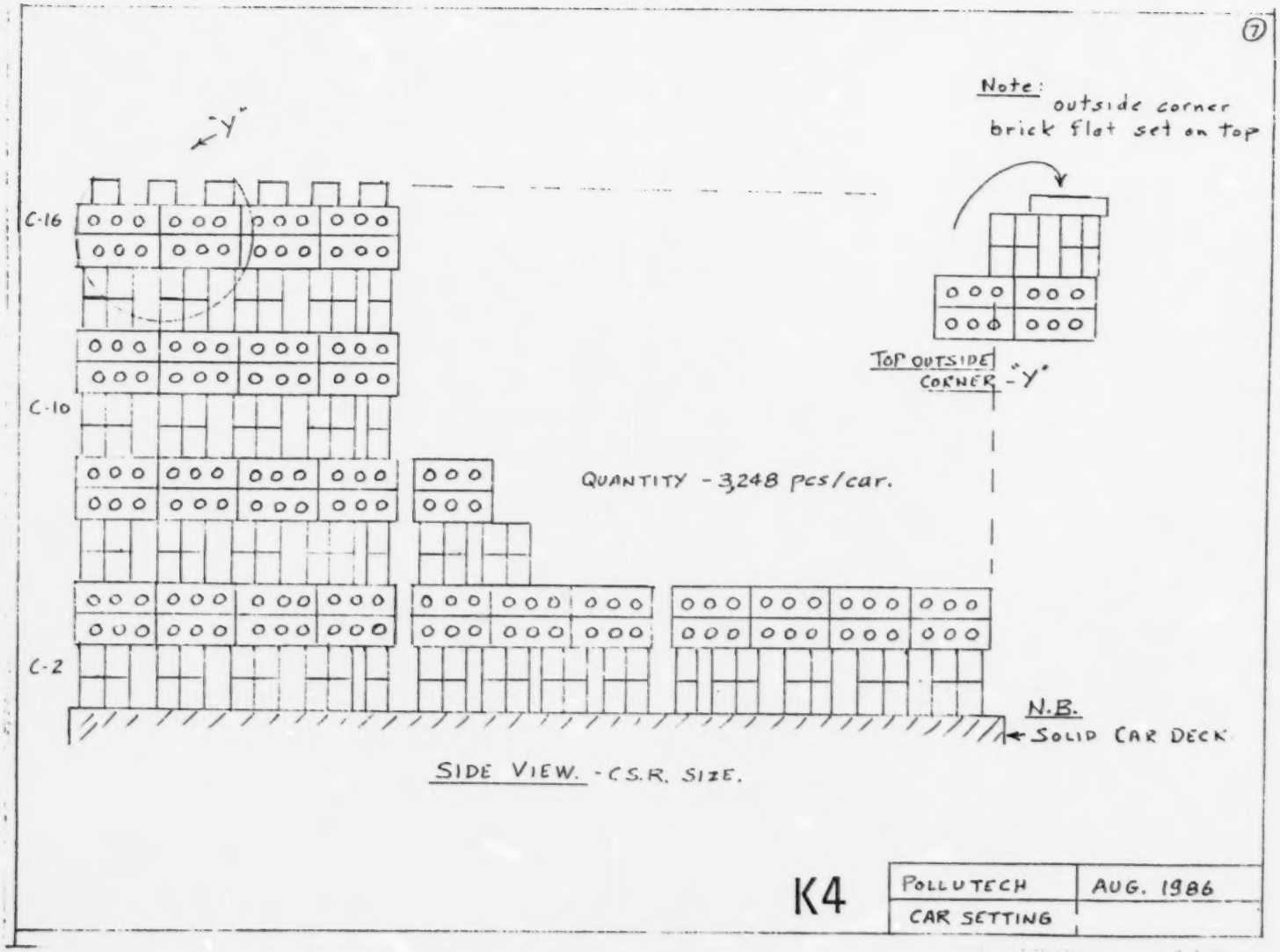
TOP VIEW C2 ROW 1

SAMPLE LOCATIONS

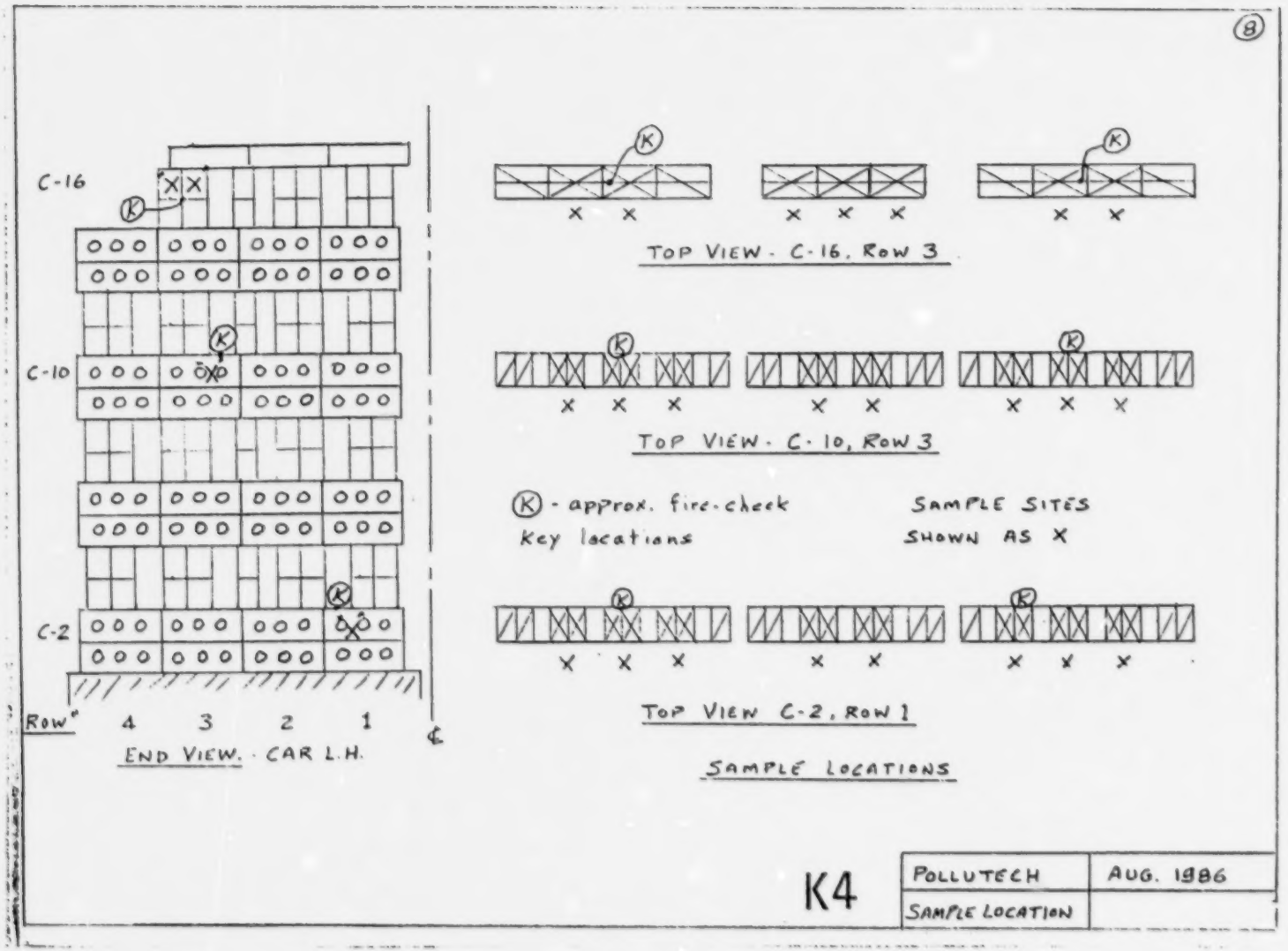
K3

POLLUTECH	JULY 1986
SAMPLE LOCATION	

POLLUTECH


7
Note: outside corner brick flat set on top
"Y"
C-16
C-10
C-2
TOP OUTSIDE CORNER - "Y"
QUANTITY - 3,248 pcs/car.
N.B.
SOLID CAR DECK
SIDE VIEW. - C.S.R. SIZE.
K4
POLLUTECH
AUG. 1986
CAR SETTING

POLLUTECH


8
C-16
C-10
C-2
Row 4 3 2 1
℄
END VIEW. CAR L.H.
TOP VIEW - C-16, ROW 3
TOP VIEW - C-10, ROW 3
(K) - approx. fire-check key locations
SAMPLE SITES SHOWN AS X
TOP VIEW C-2, ROW 1
SAMPLE LOCATIONS
K4
POLLUTECH
AUG. 1986
SAMPLE LOCATION
POLLUTECH

POLLUTECH

APPENDIX 3

Kiln Information During Firing

POLLUTECH

August 1986

Chart of Kiln Information

K1	K2		K3	K4
292' 0"	391' 10"	Kiln length	368' 0"	290' 0"
8 brick	10 brick	Width-brick	9 brick	8 brick
30	39	Cars in kiln[1]	37	30
20.57	28	Cars/24 hrs.	26	21
3,456	4,544	pcs./car[2]	3,456	3,248
71,094	127,232	pcs./24 hrs.	89,856	68,208
144.6	291.9	fired wt.[3]/24 hrs.	214.2	153.0
418.6 Mcf	745.3 Mcf	fuel used/24 hrs.	755.3 Mcf	383.2 Mcf
2.95	2.604	Btu's[4] x 10^6/ tonne	3.60	2.55
oxidizing	oxidizing/ reducing cycle	Atmosphere	oxidizing	oxidizing
485	450	P.C. Temp. F[5]	255	477
29,050 cfm @ 916 rpm	33,900 cfm @ 945 rpm	Exhaust Fan[6] rating	25,000 cfm (Est.)	24,000 cfm @750 rpm

Notes:

[1] Car spaces

[2] C.S.R. size

[3] tonnes

[4] 1020 Btu/1000 cu. ft.

[5] Products of combustion

[6] Fan ratings at 70 F and design rpm

Note:

1) Temperature readings were in most instances interpolated from kiln records during the firing of the brick samples. In addition the temperature readings are crown temperatures except where noted.

2) Exhaust volumes are shown from fan charts and/or as estimated by plant personnel from prior testing and charts.

3) Generally the temperature of the brick load in the kiln will be less than the T.C. temperatures in the heating up phase and more than the T.C. temperature in the cooling phase.

POLLUTECH

Kiln Information

Location: K1

Schedule: Kiln #1

Car #184 into kiln 2:20 a.m. - July 19, 1986
exit kiln 2:32 a.m. - July 21
Car 15 into kiln 3:30 p.m. - July 19, 1986
exit kiln 3:42 p.m. - July 21

Push rate 20.57 cars/24 hours (70 minute schedule)

Note: Cars left at exit end of kiln as long as possible

Product in kiln C.S.R. size

Tonnage, fired weight basis, through kiln

3,456 pcs/car x 20.57 (70 min./car) = 71,094 pcs.

x 2.034 Kg/pc = 144,605 kg = 144.6 tonnes/24 hrs.

Fuel Consumption as reported

7:00 a.m. July 19 to 7:00 a.m. July 20 - 418,600 cu. ft.

7:00 a.m. July 20 to 7:00 a.m. July 21 - 418,600 cu. ft.

average consumption/24 hours = 418,600 cu. ft.

Consumption per tonne = $\frac{418,600}{144.6}$ = 2,895 cu.ft./tonne

@ 1020 Btu/1000 cu.ft. = 2.95×10^6 Btu/tonne

= 3.115 GJ/tonne

Exhaust

Fan: Robinson AE 48" x 19 7/8"

Rated 29,050 cfm @ 916 rpm, 7" S.P. cold, 3.86 S.P. hot

Motor 50 hp, rated 31.4 hp hot. Op. temp. 500 F

Note: Fired weight based on samples of bulk brick taken from cars 184 and 15.

Average exhaust gas temperature 485 F

Volume: 11,900 cfm @ 440°F measured

Kiln

Swindell Dressler

Length - 292' 0"

Kiln car - 9' 4" long

Car spaces in kiln 31

K1 - Kiln 1

Thermocouple No.	Accumulated Time	T.C. Temperature (F) at car #184	#15
TC 1	.7 hrs.	705 F	710 F
TC 2	2.5	920	920
TC 3	4.3	1100	1100
TC 4	7.0	1280	1280
TC 5	9.2	1370	1370
TC 6	11.6	1440	1440
TC 7	13.5	1590	1590
TC 8	15.2	1715	1715
TC 9	17.0	1860	1854
TC 10	18.9	1958	1956
TC 11	20.6	1954	1952
TC 12	22.5	1848	1847
TC 13	23.8	1510	1510
TC 14	26.6	1300	1300
TC 15	28.7	940	935
TC 16	30.8	490	485
TC 17	33.0	390	380

P.C. 480 - 495 485

Notes: Thermocouples located in centre of arch or flat roof. P.C. fan temperatures are average for period. Temperatures at TC 11-13 locations are average of optical readings taken on the load. Strip chart showed normal temperature variations in firing zone, i.e.: plus/minus 10 F

POLLUTECH

Kiln Information

Location: **K2**

Schedule: Kiln #2

Car #137 into kiln 11:15 p.m. - July 22, 1986
exit kiln 9:40 a.m. - July 24

Car 301 into kiln 12:09 a.m. - July 23, 1986
exit kiln 10:35 a.m.- July 24

Push rate 28 cars/24 hours

Note: Exit times approximate

Product in kiln C.S.R. size

Tonnage, fired weight basis, through kiln

4,544 pcs/car x 28 = 127,232 pcs.

x 2.294 Kg/pc = 291,870 kg = 291.9 tonnes/24 hrs.

Fuel Consumption as reported

Gas totalizer reading 11:15 p.m. July 22 - 102498420
reading 9:40 a.m. July 24 - 102528680
for 34 hours, 25 minutes; used 30,260 m^3

Average consumption per 24 hours = 21,105 m^3

21,105 m^3 x 35.31476 = 745,318 cu. ft.

Consumption per tonne = $\frac{745,318}{291.9}$ = 2,553 cu.ft./tonne

@ 1020 Btu/1000 cu.ft. = 2.604×10^6 Btu/tonne

= 2.748 GJ/tonne

Exhaust

Fan: Robinson "48" AE-6-BB

Rated 33,900 cfm @ 945 rpm, 7" S.P. cold

Motor 50 hp.

Amp reading 35A (70%)

Exhaust (cont'd.)

Draft in firing zone -.04" H_2O
O_2 in firing zone 8.0%
Average exhaust gas temperature 450 F

Kiln

Harrop Ceramic Services
Length - 391' 10"
Kiln car - 9' 8" long
Car spaces in kiln 40

K2 - Kiln 2

Thermocouple No.	Accumulated Time	T.C. Temperature (F) at car #137 and 301
TC 2	1.4 Hrs.	565 F
TC 3	2.7	648
TC 5	4.2	698
TC 6	5.3	732
TC 8	6.4	817
TC 9	7.4	909
TC 10	8.5	1157
TC 11	9.5	1103
TC 13	10.6	1189
TC 15	12.9	1497
TC 17	14.0	1771
TC 18	15.3	1830
TC 20	16.5	1764
C 1	17.3	1791
C 2	19.4	1855
TC 23	20.1	1864
C 3	20.8	1891
TC 26	22.1	1742
TC 28	24.2	1479
TC 29	25.0	1441
TC 31	26.1	1164
TC 32	27.2	997
TC 33	28.3	811
TC 34	29.3	(124) u/s
TC 36	31	511
TC 38	32.8	140

Notes:

Temperatures at C1, 2 and 3 were below set points respectively 1860, 1900 and 1900.

Kiln Information

Location: K3

Schedule:

Car #160 into kiln 4:18 p.m. - July 30, 1986
exit kiln 3:30 a.m. - August 1

Car 144 into kiln 5:15 p.m.- July 30, 1986
exit kiln 4:30 a.m.- August 1

Push rate 26 cars/24 hours, exit time is approximate.

Product in kiln C.S.R. size

Tonnage, fired weight basis through kiln

3,456 pcs/car x 26 = 89,856 pcs.

x 2.384 Kg/pc = 214,217 kg = 214.2 tonnes/24 hrs.

Fuel Consumption as reported

8:00 a.m. July 29 to 8:00 a.m. July 30 - 755,392 cu. ft.
8:00 a.m. July 30 to 8:00 a.m. July 31 - 759,063 cu. ft.
8:00 a.m. July 31 to 8:00 a.m. August 1 751,485 cu. ft.
Average consumption per 24 hours = 755,313 cu. ft.

Consumption per tonne = $\frac{755,313}{214.2}$ = 3,526 cu.ft./tonne

@ 1020 Btu/1000 cu.ft. = 3.60×10^6 Btu/tonne
= 3.795 GJ/tonne

Exhaust

Plant personnel estimated fan exhausting 20,000 cfm (from prior test records)

Note: Fired weight based on samples of bulk brick taken from cars 144A and 160A.

Average exhaust gas temperature 255 F.

Kiln

Harrop Ceramic Services
Length - 368' 0" + extension at exit, overall 375' 0"
Kiln car - 9' 7" long
Car spaces in kiln 38

K3

Thermocouple No.	Accumulated Time	T.C. Temperature (F) at car #144A	#160A
TC 1	1.3 hrs.	250	275
TC 2	3.2	750	790
TC 3	4.7	820	810
TC 4	5.9	1005	1025
TC 5	7.0	1200	1200
TC 6	8.6	1350	1350
TC 7	10.3	1440	1445
TC 8	11.4	1440	1430
TC 9	12.9	1530	1530
TC 10 (C-1)	14.0	1670	1675
TC 11	15.2	1785	1785
TC 12	16.4	1760	1765
TC 13	17.5	1835	1835
TC 14 (C-2)	18.7	1880	1880
TC 15	19.8	1915	1925
TC 16	20.7	1900	1900
TC 17	21.5	1570	1570
TC 18	22.7	1590	1590
TC 19	24.5	1370	1365
TC 20	26.1	1365	1365
TC 21	27.8	1285	1285
TC 22	29.6	1190	1175
TC 23	31.3	1020	1010
TC 24	33.3	620	640

P.C. 255

POLLUTECH

Kiln Information

Location: K4

Schedule: Kiln #1

Car #2006 into kiln 12:00 midnight - August 7, 1986
exit kiln 9:10 a.m.- August 9
Car 769 into kiln 1:10 a.m.- August 8, 1986
exit kiln 10:15 a.m. - August 9

Push rate 21 cars/24 hours Cars left at exit end of kiln until well clear of kiln

Product in kiln C.S.R. size

Tonnage, fired weight basis, through kiln

3,248 pcs/car x 21 = 68,208 pcs.

x 2.243 Kg/pc = 152,990 kg = 153.0 tonnes/24 hrs.

Fuel Consumption as reported

For 36 hour period including time cars were in kiln meter reading 574,750 cu. ft. (corrected)

Average consumption/24 hrs. = 383,167 cu. ft.

Consumption per tonne = $\frac{383,167}{153.0}$ = 2,504 cu.ft./tonne

@ 1020 Btu/1000 cu.ft. = 2.55×10^6 Btu/tonne

= 2.695 GJ/tonne

Exhaust

Fan: Robinson AE6 BB 44" x 18¾ @ 755 rpm.

Rated 24,000 cfm @ 3.0 S.P. (750 rpm), drawing 25 Amp.

Note: Fired weight based on samples of bulk brick taken from cars 2006 and 769.

Exhaust (cont'd.)

Average exhaust gas temperature 477 F

Kiln

Harrop Ceramic Services

Length - 290' 0"

Kiln car - 9' 6" long

Car spaces in kiln 30

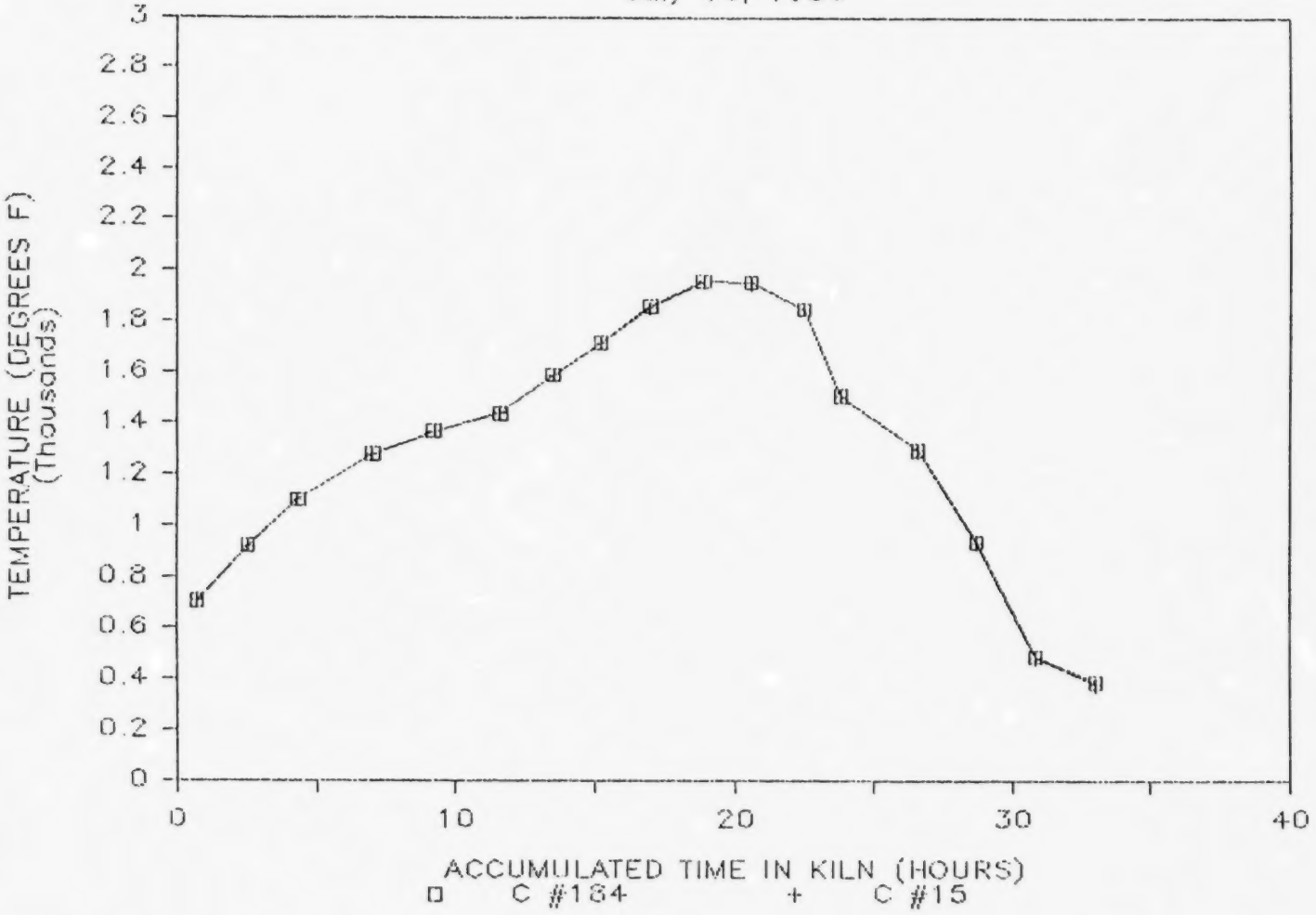
K4

Thermocouple No.	Accumulated Time	T.C. Temperature (F) at car #2006	#769
TC 2	2.2 Hrs.	674	655
TC 6	6.2	883	884
TC 7	8.1	998	997
TC 10	11.0	1245	1239
TC 11	12.8	1477	1473
TC 14	15.6	1615	1608
TC 15	16.8	1695	1701
TC 16	17.9	1754	1748
TC 17	19.3	1825	1822
TC 18	20.8	1900	1900
TC 20	22.2	1930	1928
TC 21	24.3	u/s	u/s
TC 22	25.1	note	note
TC 24	27.2	1600	1617
TC 26	30.1	1097	1105
TC 29	32.9	524	527

Note: TC 22 not read. However temp. 1745 on next log approximately 8 hours later

K1 — KILN 1 TEMPERATURE PROFILE

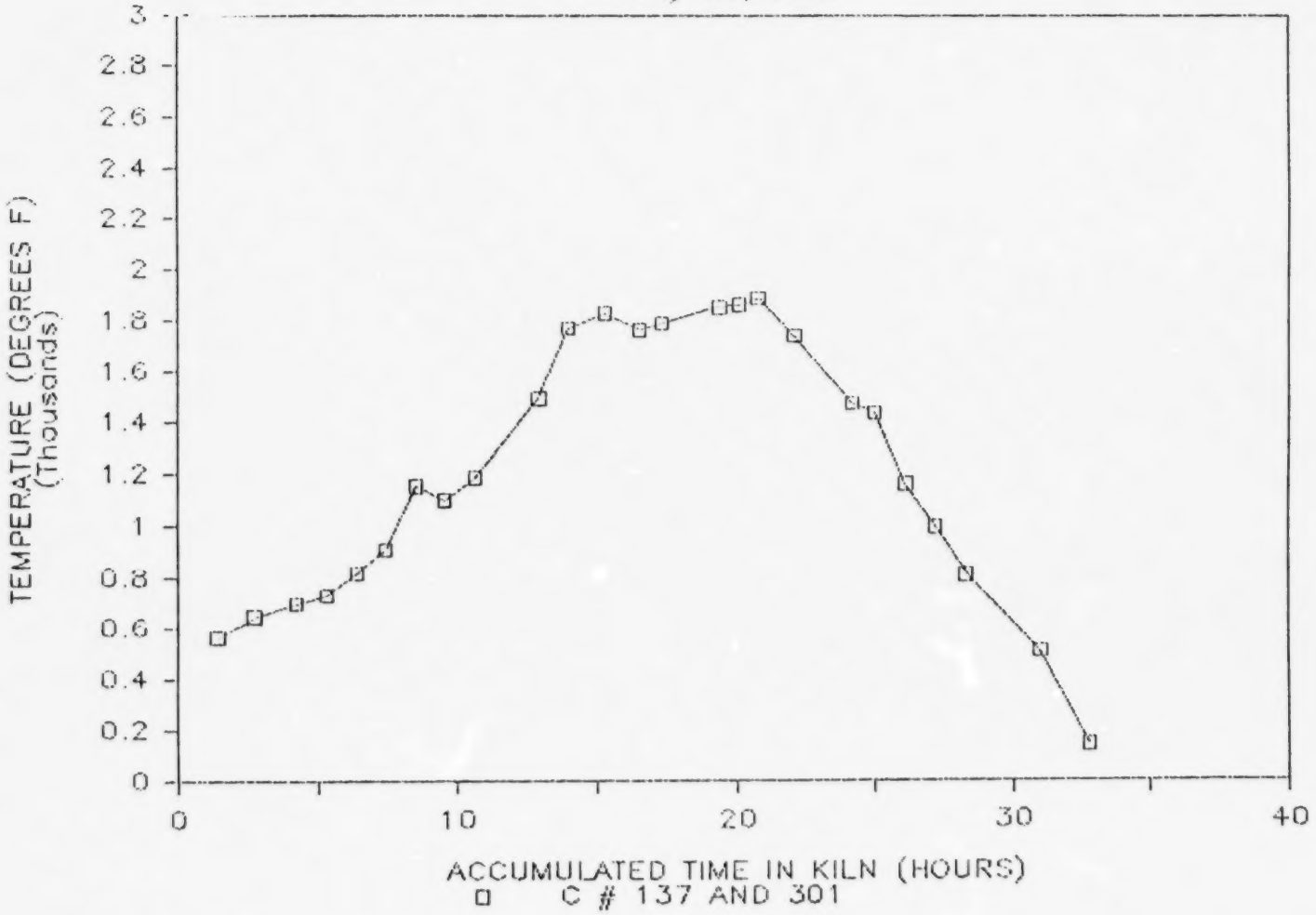
July 16, 1986



POLLUTECH

K2 — KILN 2 TEMPERATURE PROFILE

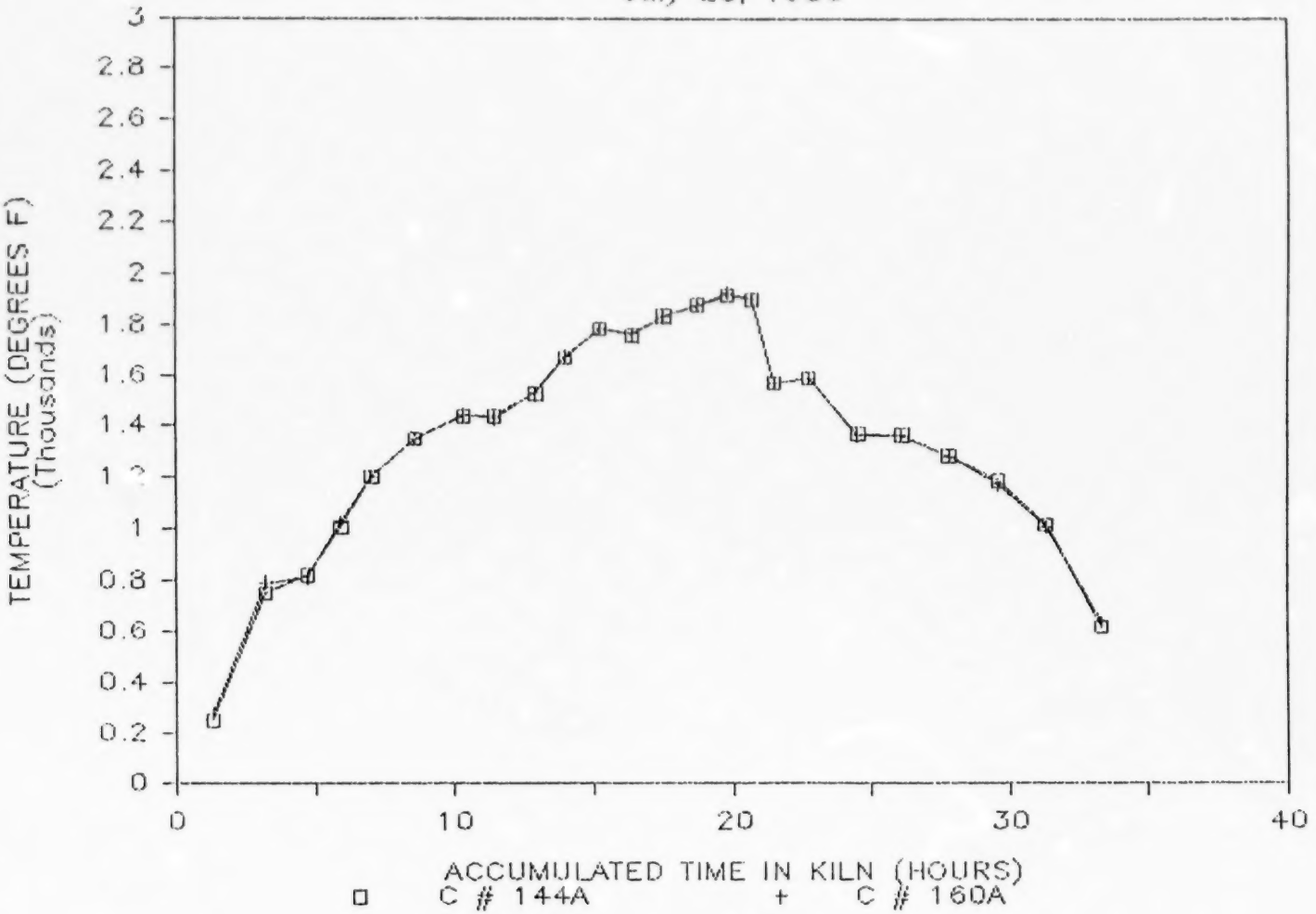
July 21, 1986



POLLUTECH

K3 — KILN TEMPERATURE PROFILE

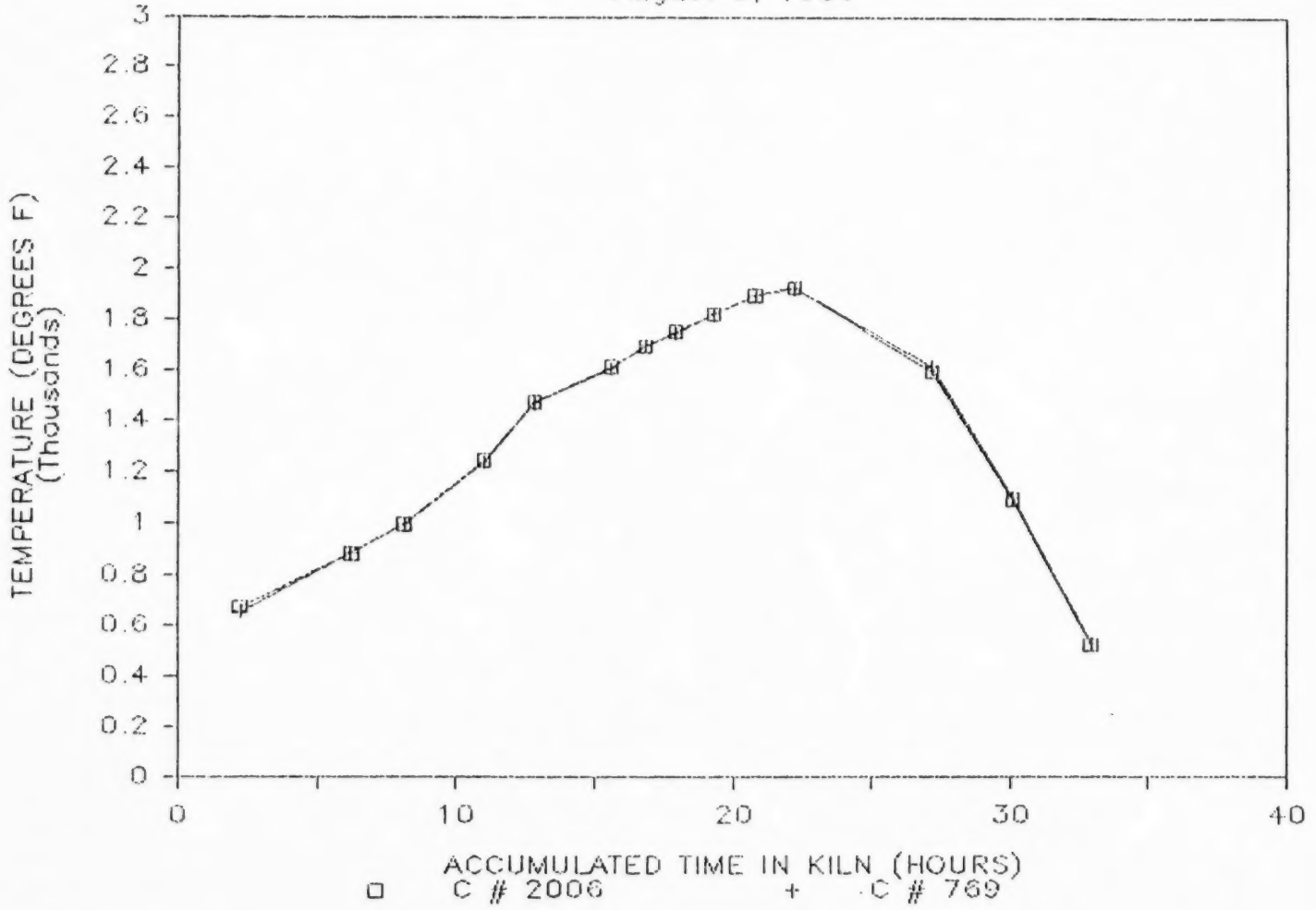
July 28, 1986



POLLUTECH

K4 — KILN TEMPERATURE PROFILE

August 5, 1986



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